

# Tobermorite ion-exchanger from paper recycling ash and waste glass

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**1. Introduction** – 11 Å tobermorite ( $\text{Ca}_5(\text{Si})_6\text{O}_{16}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ ) and its Al-substituted counterpart are layer-lattice cation-exchangers that are of interest with respect to their applications in nuclear and hazardous wastewater treatment [1-3]. In 2015, the European Declaration on Paper Recycling reported that 71.5% of all paper consumed in Europe was recycled, corresponding to 1.2 million tonnes more than their 70% target [4]. Waste paper recycling ash (PRA) arising from this activity contains reactive calcium aluminosilicate phases that can be used for the hydrothermal synthesis of tobermorite when stoichiometrically adjusted with additional silicate-bearing reagents [1]. Waste soda-lime-silica container glass (SCG) has also been used as a partial feedstock for the preparation of tobermorite in alkaline media [2]. This research tested the feasibility of a one-step synthesis of tobermorite from a combination of PRA and SCG under alkaline hydrothermal conditions at 100 °C. Reaction products were analysed by powder X-ray diffraction (XRD) and scanning electron microscopy (SEM). This study also evaluated the  $\text{Cs}^+$  cation-exchange capacity (CEC), selective  $\text{Cs}^+$  distribution coefficients ( $K_d$ , from  $\text{Na}^+$  and  $\text{Ca}^{2+}$  background solutions) and the uptake kinetics of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  by the waste-derived tobermorite product.

**2. Experimental** – PRA (Aylesford Newsprint, Kent, UK) and SCG were ground to pass 250  $\mu\text{m}$ . To prepare the tobermorite, 3.5 g of PRA, 3.5 g of SCG and 2.35 g of CaO were mixed with 60  $\text{cm}^3$  of 4 M  $\text{NaOH}_{(\text{aq})}$ , sealed in a PTFE autoclave and heated at 100 °C for 1, 2 and 5 days. Solid reaction products were separated by filtration, washed to pH ~8 with deionised water and dried in air at 60 °C prior to characterisation by XRD and SEM.  $\text{Cs}^+$  CEC of the final 5-day tobermorite product was determined by the saturation of the ion-exchange sites with  $\text{K}^+$  ions and their subsequent displacement by  $\text{Cs}^+$  ions at 25 °C [1].  $\text{Cs}^+$  selectivity was evaluated by the uptake of  $\text{Cs}^+$  from solutions having molar ratios  $[\text{Cs}^+]:[\text{Na}^+]$  or  $[\text{Cs}^+]:[\text{Ca}^{2+}]$  equal to 1:100 [1].  $K_d$  values were calculated as the ratio of the amounts of  $\text{Cs}^+$  sorbed and  $\text{Cs}^+$  remaining in solution (in  $\text{cm}^3/\text{g}$ ) [1]. Uptake kinetics of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  were determined by exposure of 50 mg of tobermorite product to 200  $\text{cm}^3$  of 0.5 mM metal nitrate solution for up to 24 h [3]. All solutions were analysed by atomic absorption spectroscopy. All preparations and analyses were carried out in triplicate.

**3. Results and Discussion** - PRA comprises gehlenite ( $\text{Ca}_2\text{Al}_2\text{SiO}_7$ ), åkermanite ( $\text{Ca}_2\text{MgSi}_2\text{O}_7$ ),  $\beta$ -dicalcium silicate ( $\text{Ca}_2\text{SiO}_4$ ), anorthite ( $\text{CaAl}_2\text{Si}_2\text{O}_8$ ) and an amorphous silicate phase [1]. XRD analysis indicated that, during the hydrothermal reaction with SCG, the constituent mineral phases of PRA are progressively replaced by 11 Å tobermorite with hydrogarnet as a minor phase. SEM images confirmed that the product particles were in the size range 2 – 50  $\mu\text{m}$  and displayed the typical foliaceous morphology of tobermorite.  $\text{Cs}^+$  CEC of the tobermorite product was found to be  $59 \pm 4$  meq/100g, and  $K_d$  values were  $574 \pm 13$  and  $658 \pm 34$   $\text{cm}^3/\text{g}$  from  $\text{Na}^+$  and  $\text{Ca}^{2+}$  background solutions, respectively. The sorption of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  ions followed pseudo-second order kinetics with maximum uptake values of  $130 \pm 4$  and  $357 \pm 7$  meq/100g, respectively, at 24 h.

**4. Conclusions** - A candidate  $\text{Cs}^+$ -selective tobermorite cation exchanger with a high uptake-capacity for  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  ions can be prepared by a facile one-step hydrothermal reaction between paper recycling ash and waste container glass.

## 5. References

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