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

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**1. Introduction** – 11 Å tobermorite  $(Ca_5(Si)_6O_{16}(OH)_2.4H_2O)$  and its Al-substituted counterpart are layerlattice 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 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 Cs<sup>+</sup> cation-exchange capacity (CEC), selective Cs<sup>+</sup> distribution coefficients (K<sub>d</sub>, from Na<sup>+</sup> and Ca<sup>2+</sup> background solutions) and the uptake kinetics of Cd<sup>2+</sup> and Pb<sup>2+</sup> by the waste-derived tobermorite product.

**2. Experimental** – PRA (Aylesford Newsprint, Kent, UK) and SCG were ground to pass 250  $\mu$ 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 cm<sup>3</sup> of 4 M NaOH<sub>(aq)</sub>, 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. Cs<sup>+</sup> CEC of the final 5-day tobermorite product was determined by the saturation of the ion-exchange sites with K<sup>+</sup> ions and their subsequent displacement by Cs<sup>+</sup> ions at 25 °C [1]. Cs<sup>+</sup> selectivity was evaluated by the uptake of Cs<sup>+</sup> from solutions having molar ratios [Cs<sup>+</sup>]:[Na<sup>+</sup>] or [Cs<sup>+</sup>]:[Ca<sup>2+</sup>] equal to 1:100 [1]. K<sub>d</sub> values were calculated as the ratio of the amounts of Cs<sup>+</sup> sorbed and Cs<sup>+</sup> remaining in solution (in cm<sup>3</sup>/g) [1]. Uptake kinetics of Cd<sup>2+</sup> and Pb<sup>2+</sup> were determined by exposure of 50 mg of tobermorite product to 200 cm<sup>3</sup> 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 (Ca<sub>2</sub>Al<sub>2</sub>SiO<sub>7</sub>), åkermanite (Ca<sub>2</sub>MgSi<sub>2</sub>O<sub>7</sub>), βdicalcium silicate (Ca<sub>2</sub>SiO<sub>4</sub>), anorthite (CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>) 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. Cs<sup>+</sup> CEC of the tobermorite product was found to be  $59 \pm 4 \ \text{meq}/100g$ , and K<sub>d</sub> values were  $574 \pm 13 \ \text{and} \ 658 \pm 34 \ \text{cm}^3/\text{g}$  from Na<sup>+</sup> and Ca<sup>2+</sup> background solutions, respectively. The sorption of Cd<sup>2+</sup> and Pb<sup>2+</sup> ions followed pseudo-second order kinetics with maximum uptake values of  $130 \pm 4 \ \text{and} \ 357 \pm 7 \ \text{meq}/100g$ , respectively, at 24 h.

**4. Conclusions -** A candidate  $Cs^+$ -selective tobermorite cation exchanger with a high uptake-capacity for  $Cd^{2+}$  and  $Pb^{2+}$  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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