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Synthesis and characterisation of mesoporous silica phases containing heteroatoms, and their cation exchange properties. Part 3. Measurement of distribution coefficients for uptake of 137-Cs, 89-Sr and 57-Co radioisotopes

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ABSTRACT

Well characterised tunable [1] MCM-41 phases with differing pore structures and containing aluminium, boron and zinc heteroatoms were described in Part 1 [2] to this series. Part 2 [3] illustrated that representative phases exhibited cation exchange selectivity.

This part of the series studied the ability of 27 of the phases to take up the environmentally harmful radioisotopes of caesium, cobalt, and strontium, assessed by the measurement of distribution coefficients.

Measurements were made in deionised water to simulate ground waters, with 0.1 M HNO_3, 0.1 M $NaNO_3$, and 0.1 M HNO_3/NaOH solutions, chosen as nuclear waste simulants. In addition the effect of sodium tetraborate and tri-sodium citrate (10^{-3} to 10^{-6} M) on 57-cobalt uptake was studied. These additives were chosen as relevant to decommissioning/general decontamination (citrate) and Boiling Water or Pressurised Water reactors (borate) encompassing their potential to form complex ions with elements such as cobalt.

1. Introduction

The possibility of the creation of mesoporous materials of tuneable structure, morphology and composition has recently been reviewed by Yang et al. [1].

This potential flexibility was the emphasis in the syntheses of several phases of the mesoporous material MCM-41 containing aluminium, boron and zinc, described in Part 1 of this series, as potential cation-exchange media [2]. The syntheses used trimethyl ammonium bromide detergents of C_{8-16} chain lengths as templates.

All phases were characterised by traditional elemental analyses, PXRD, MASNMR, and nitrogen porosimetry [2]. Part 2 of the series [3] demonstrated that representative phases showed useful cation exchange selectivity.

This work continued the investigation of these materials as potential exchangers for the clean-up of aqueous nuclear wastes which contain caesium, cobalt and strontium radioisotopes as common components as well as other, more complex, wastes.

Measurements were made in deionised water to simulate ground waters, with 0.1 M HNO_3, 0.1 M $NaNO_3$, and 0.1 M HNO_3/NaOH solutions, chosen as nuclear waste simulants. In addition the effect of sodium tetraborate and tri-sodium citrate (10^{-3} to 10^{-6} M) on 57-Co uptake was studied. They were relevant to Boiling Water or Pressurised Water reactors (borate) and decommissioning/general decontamination (citrate) with their potential to form complex ions with elements such as cobalt [4].

The efficacy of the MCM-41 phases has been quantified by the estimation of distribution coefficients.

2. Experimental

2.1. Materials

A total of 27 MCM-41 phases was examined. Of these, five were pure silica [Si MCM-41C_X], eight contained aluminium [Al(Z)MCM-41C_X], six boron[B(Z)MCM-41C_X] and eight zinc[Zn(Z)MCM-41C_X], where *Z* represents Si/metal oxide ratio used in the original synthesis gel, and C_X the template chain length. In addition an Al(50)B(13) MCM-41C_{16} phase was included. All materials were used in their "as synthesised" forms and contained both sodium and H_3O^+ cations [3]. Salt solutions used were nitrates of at least 99% purity dissolved in deionised water. Radioisotopes were supplied by Amersham International UK. Radioisotope activity was determined using liquid scintillation counting employing an Aquasafe 300™ cocktail [3].

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Table 1
Simulant solutions.

Solution	pH	Simulant
Deionised water	~6	Ground water
0.1 M HNO_3	1	Decontamination/decommissioning waste
0.1 M $NaNO_3$	~4.4	Neutralised decontamination/ decommissioning waste
0.1 M $NaNO_3$/NaOH	13	Pond water or alkaline decontamination/ decommissioning waste

Table 1 details the different solutions used and the wastes they simulate. The solutions were prepared with spikes such that the count rate was approximately 10,000 cpm/mL in the final solution. Sodium tetraborate and tri-sodium citrate (10^{-3} to 10^{-6} M) additions were made to 57-cobalt solutions in deionised water.

2.2. Cation exchange capacities

An approximate estimate of the cation exchange capacities of the materials studied was possible by relating the mass loss from the detergent template, taken from thermogravimetric analysis, to the number of charge equivalents. This proved to be problematic due to the uncertainty of the extent of the mass loss peaks.

The characterisation of the materials studied showed that atomic absorption analyses of their sodium contents did not necessarily reflect their exchange capacities because of the presence of sodium cations which did not occupy cation exchange sites [2,3].

Because of these difficulties the labile sodium cations present were labelled with the radioisotope 22-Na thus enabling an accurate estimate of cation exchange capacity by using the isotope dilution technique.

2.3. Measurement of distribution coefficients (K_d)

Approximately 0.0300 g (±0.0002 g) aliquots of the MCM-41 phases were accurately weighed and separately brought into contact with 6 mL of the solutions, described above, in 15 mL polypropylene centrifuge tubes. The suspensions produced were equilibrated, end-over-end, in a mineralogical roller for 24 h, which was the period previously determined as that sufficient to achieved equilibrium. At equilibrium the suspensions were centrifuged at 4000 rpm for 20 min. The supernatants were filtered through polyvinylidine fluoride filters of pore size 0.4 µm, except those solutions containing the isotope 57-Co, and those in deionised water, as these were found to be liable to strong isotopic adsorption by the filters.

One milliliter aliquots were analysed for radioactivity. Small portions of the equilibrium supernatants were retained for pH analysis using a pre-calibrated Orion 720A pH meter with an Accumet semi-micro calomel electrode.

Distribution coefficients were calculated from the following:

$$K_d = (A_0 - A)/A \cdot V/m, \tag{1}$$

where K_d = distribution coefficient (L/kg), A_0 = initial activity (Bq/mL), A = equilibrium activity (Bq/mL), V = volume of solution (L), and m = mass of material (kg) contacted with V.

All K_d measurements were in at least triplicate, and quoted as mean values. A full error analysis showed that they were subject to a maximum error of ±10%.

3. Results and discussion

3.1. Cation exchange capacities

The CEC values, measured radiometrically, were as listed in Table 2.

Table 2
Cation exchange capacities (CEC) meq g^{-1}, and equilibrium pHs of MCM-41 materials.

MCM-41	CEC	pH	MCM-41	CEC	pH
Si(100)C_{16}	0.29	8.86	B(50)C_{16}	0.37	8.80
Si(100)C_{14}	0.26	9.07	B(50)C_{14}	0.38	8.99
Si(100)C_{12}	0.27	8.99	B(50)C_{12}	0.35	8.92
Si(100)C_{10}	0.25	9.08	B(50)C_{10}	0.28	8.92
Si(100)C_8	0.25	9.16	B(50)C_8	0.26	9.23
			B(13)C_{16}	0.24	8.86
Al(100)C_{16}	0.36	8.66	Zn(100)C_{16}	0.27	8.84
Al(50)C_{16}	0.53	7.28	Zn(50)C_{16}	0.32	8.78
Al(50)C_{14}	0.55	7.85	Zn(50)C_{14}	0.84	9.12
Al(50)C_{12}	0.75	8.99	Zn(50)C_{12}	0.40	8.91
Al(50)C_{10}	0.77	8.84	Zn(50)C_{10}	0.40	9.21
Al(50)C_8	0.83	9.15	Zn(50)C_8	0.46	9.42
Al(25)C_{16}	0.55	7.29	Zn(25)C_{16}	0.31	8.79
Al(13)C_{16}	0.53	9.10	Zn(13)C_{16}	0.29	8.50
Al(50)B(13)C_{16}	0.74	8.54			

Note: Bracketed figures refer to molar ratios of Si:MeO_X in the synthesis gel , where M = B, Al, Zn, and C_X is the detergent (TMA^+Br^-) chain length.

3.1.1. Si-MCM-41 phases

The CEC decreased fractionally with detergent chain length which reflected a coincident decrease in ionisable hydroxyl groups as the interconnectivity within the silica framework increased. The small, generalised, increase in pH can be linked to the same decrease in OH groups.

3.1.2. B-MCM-41 phases

As in the wholly silica materials, there was a decrease in CEC as the chain length decreased commensurate with the presence of fewer hydroxyl groups – mirrored by the increased pH values.

If a straight comparison to the silica based MCM-41 materials can be made, the higher CEC values seen when longer chain length templates were used might be taken as evidence of some boron activated sites. The lower value of CEC seen when there was a smaller amount of boron in the initial synthesis supported this.

3.1.3. Al-MCM-41 phases

When the amount of aluminium in the synthesis gel was constant (at 50) progressive increases of CEC were observed as the template chain length shortened, indicative of the insertion of Al into the MCM-41 silica framework as has been noted in both Part 1 [2] and Part 2 [3] in this series. The increases in CEC coincided with an increase in pH.

It should be noted that the molar ratio of Si:Al of 50 seemed to be an optimum value for a high CEC, as the materials produced from gels with differing ratios (higher and lower) had lower CECs when using the same (C_{16}) detergent.

The sample made with a C_{16} gel containing both Al and B had a comparatively higher capacity than an equivalent one without B. This interesting observation warranted further investigation but was not pursued in this work.

3.1.4. Zn-MCM-41 phases

The CEC and pH values followed the same pattern as those for the Al phases-with Zn(50)C_{14} being an exception. It could be argued that materials containing Si and B made from the C_{14} template also showed anomalies which may mean that the starting material contained an impurity. Once again the mole ratio of 50 seemed optimal.

If Zn^{2+} was in tetrahedral interstices in the silicon–oxygen MCM-41 framework, comparison to materials with Al^{3+} similarly isomorphously substituted should impart a higher cation capacity when Zn was present. This was not so with Zn containing materials as they had approximately one half of the CECs of the Al-MCM-41