

A high throughput screening method for the selection of zeolites for binding cations†

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An effective high throughput screening technique is described for the rapid analysis of zeolites as binding agents for cationic sequestration.

The use of pillared clays and zeolites for the trapping and sequestration of cations has been studied for many years. While the binding of any specific cation within zeolites can be determined by a systematic study or even combinatorial methods, it is a challenge to selectively predict the extraction of a particular cation from complex mixtures, for example nuclear waste. In recent years, Micro X-Ray Fluorescence (MXRF) has proven useful as an effective screening technique for a number of combinatorial chemistry applications.¹ We were interested in the selective extraction of metal cations from complex mixtures at a variety of pH values. In particular, the removal of cesium from systems with high concentrations of competing metals such as Ca²⁺, Na⁺, Al³⁺ and Fe³⁺, as well as a number of possible organic cations and surfactants. Zeolites appeared to have many of the properties we desired. While binding data for specific metals in zeolites is available,² competitive information is difficult to obtain. MXRF is a rapid, sensitive technique which provides quantitative screening of zeolite–metal binding, and can be carried out with all competing contaminants present. This study demonstrates the applicability of MXRF in determining the most selective sequestering zeolite for a specific cation from a complex mixture of species.

A range of naturally occurring and synthetic cesium binding zeolites was studied including: Valfor CP-805 (synthetic, zeolite beta), Zeolyst[™] CBV 21A (synthetic, mordenite), LZ-210 (synthetic, faujasite), SAPO-34 powder (synthetic), clinoptilolite (natural), Zeolyst[™] CBV-90A (synthetic, H-mordenite), ZSM-5 40 (synthetic, ZSM-5), Beta powder (synthetic, zeolite beta), mordenite (natural), Zeolyst[™] CBV-300 (synthetic, ammonium-Y) and ZSM-5 25 (synthetic, ZSM-5). A solution was prepared containing the following metals: Co, Cs, Ca, Al, Fe, Ir, Sr, Mn, Mg, Na and K (High Purity Standards, Charleston, NC). This mixed metal solution represented the potential components that may be encountered during the extraction of ¹³⁷Cs from a surface such as concrete at pH 10.

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† Electronic supplementary information (ESI) available: ¹³³Cs Magic-Angle Spinning spectra for cesium loaded zeolite/molecular sieve materials. See <http://dx.doi.org/10.1039/b506044c>

X-ray excitation and detection were performed using an EDAX Eagle II MXRF system with an Rh target excitation source and a SiLi detector (EDAX, Mahwah, NJ). The X-ray source was equipped with a polycapillary focusing optic of 50 μm nominal X-ray spot size (XOS, Albany, NY). X-ray tube operating conditions were maintained at 40 kV and 300 μA. A 256 × 200 pixel array was analyzed with a 100 ms dwell time. The integration time of individual spectra was 100 live detector seconds. Table 1 lists the element emission lines that were monitored in this study and their energies. The presence and location of the Cs⁺ cation in the zeolite was confirmed by ¹³³Cs NMR.†

Candidate zeolites (0.05 g) were immersed in a turbid mixed metal solution (Co, Cs, Ca, Al, Fe, Ir, Sr, Mn, Mg, Na and K; 7 mM of each; pH 10) (1.5 mL) and mixed for 12 h. After this time, the zeolite was filtered by gravitational filtration, washed three times with de-ionized water (15 mL) and air dried for 12 h. The dried zeolite was immobilized onto a glass slide in an indexed array, alongside a sample of the untreated zeolite. A 1.5 × 1.5 mm area at the intersection of the reacted and unreacted zeolite was analyzed. Emission lines were monitored for all elements listed in Table 1, including Cs. For this study, the ideal candidate zeolites would be those that preferentially bound Cs over all of the interference elements.

The effective Cs uptake in a particular zeolite (Fig. 1a) can be visualized in the Cs scan of its sample (as in Fig. 1b). As the color intensity of the Cs scan is proportional to its concentration, one can quickly ascertain which zeolite contains the highest relative amounts of Cs. By employing point scans (40 kV, 300 μA, integration time 100 s) on a random area of the reacted and unreacted sample, any change in intensity of the Cs L α line, ΔI , can be attributed to a change in concentration of Cs, *i.e.* the difference between the count rate of the reacted and unreacted sample (Fig. 1c and Table 2). According to our results, the zeolites that were most suitable for our application were SAPO-34 followed by Valfor CBV-300 Type Y (a synthetic analog of the

Table 1 Elemental emission lines monitored in this study

Element	Emission line	Energy/keV
Cs	L–M _{4,5} (L α)	4.29
Co	K–L _{2,3} (K α)	6.92
Ca	K–L _{2,3} (K α)	3.69
Al	K–L _{2,3} (K α)	1.49
Mn	K–L _{2,3} (K α)	5.89
Sr	K–L _{2,3} (K α)	14.14
Na	K–L _{2,3} (K α)	1.04
K	K–L _{2,3} (K α)	3.31
Mg	K–L _{2,3} (K α)	1.25
Ir	L–M _{4,5} (L α)	9.17
Fe	K–L _{2,3} (K α)	6.40

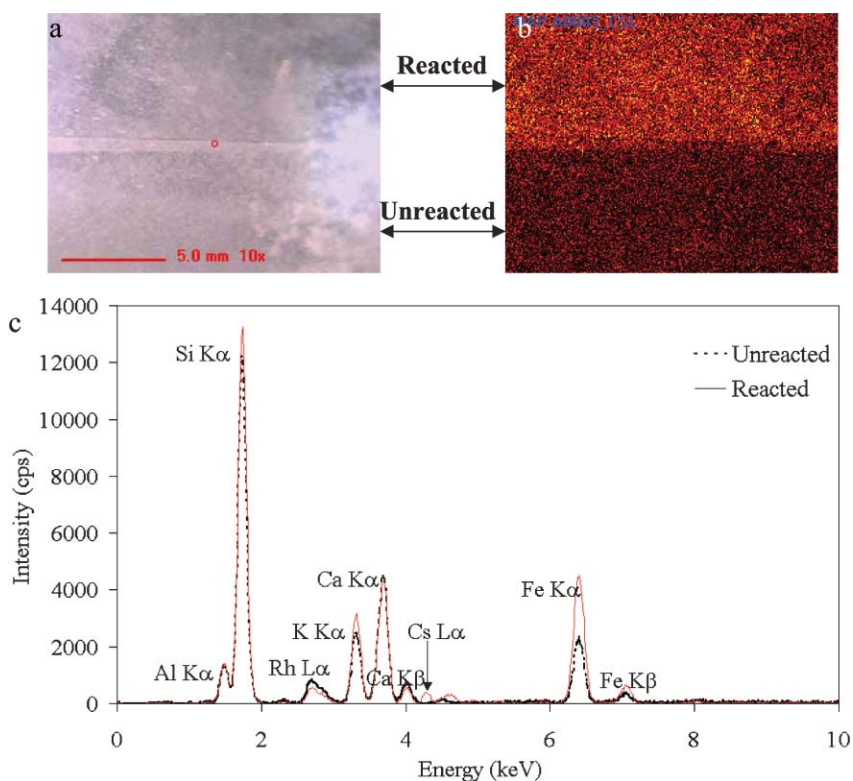


Fig. 1 (a) The optical image of the area analyzed, showing both reacted and unreacted sample. (b) The fluorescence image showing Cs uptake in the reacted sample. (c) A slight increase in the Cs L α intensity is observed when comparing the point spectra of reacted and unreacted samples.

natural zeolite faujasite) and then Clinoptilolite. The selectivity of these zeolites to Cs⁺ over the other metals studied is highlighted in Table 3. The relative increase in ΔI before and after the exposure of the zeolite to the metals indicates a preference for Cs⁺ binding in these zeolites under the given experimental conditions.

In order to determine how the Cs was bound to the zeolite, ¹³³Cs NMR experiments were conducted. According to the literature,³ a broad signal should indicate that the Cs is fixed in the lattice structure of the zeolite, whereas a narrow peak indicates the presence of a hydrated Cs, which is more loosely bound to it. In all cases the zeolites, selected by the double combinatorial study, showed the Cs cation was bound internally in them.

The method described here is an ultra rapid technique, comparable in efficiency to high throughput screening of biological samples.

Table 2 Cs uptake for various zeolites observed through the increase in Cs L α intensities

Zeolite	Intensity of Cs _{unreacted} L α /cps	Intensity of Cs _{reacted} L α /cps
Valfor CP-805	0.375	16.22
Zeolyst CBV 21A	— ^a	— ^a
L2-210	0.00	7.60
Valfor CBV-300	0.00	25.41
Clinoptilolite	0.40	15.72
Zeolyst CBV 90A	0.00	5.11
ZSM-5 40	— ^a	— ^a
Beta Powder	0.11	14.17
Mordenite	0.11	2.03
SAPO -34	0.32	33.41
ZSM-5 25	— ^a	— ^a

^a Sample decomposed under the high pH conditions.

Table 3 Selective binding of Cs over other metals

Element	$\Delta I/\text{cps}^a$		
	Valfor CBV-300	Clinoptilolite	SAPO-34
Cs	25.4	15.7	33.1
Co	0.7	1.5	5.3
Mn	1.4	0.3	2.5
Sr	1.8	0.6	0.3
Mg	0.6	1.3	2.3
Ir	0	0.4	0.3
Fe	1.5	1.9	5.6
Cr	0	0.2	0.3
Pb	0.5	0.3	0.3

^a ΔI is the relative increase in intensity.

A range of target samples were screened against a selection of solutions under the desired experimental conditions. The optimum zeolite for the removal of Cs⁺ for our application was obtained. In this way, the selection of a suitable zeolite for a particular application may now take only a couple of hours instead of weeks.

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Notes and references

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