

SANDIA REPORT

SAND2016-0521

Unlimited Release

Printed January 20, 2016

Evaluation of Strontium Selectivity by Sandia Octahedral Molecular Sieves (SOMS)

Mark J. Rigali and Thomas A. Stewart

Prepared by
Sandia National Laboratories
Albuquerque, New Mexico 87185-0747

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Approved for public release; further dissemination unlimited.



Sandia National Laboratories

Issued by Sandia National Laboratories, operated for the United States Department of Energy by Sandia Corporation.

NOTICE: This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government, nor any agency thereof, nor any of their employees, nor any of their contractors, subcontractors, or their employees, make any warranty, express or implied, or assume any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represent that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government, any agency thereof, or any of their contractors or subcontractors. The views and opinions expressed herein do not necessarily state or reflect those of the United States Government, any agency thereof, or any of their contractors.

Printed in the United States of America. This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from

U.S. Department of Energy
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831

Telephone: (865) 576-8401
Facsimile: (865) 576-5728
E-Mail: reports@osti.gov
Online ordering: <http://www.osti.gov/scitech>

Available to the public from

U.S. Department of Commerce
National Technical Information Service
5301 Shawnee Rd
Alexandria, VA 22312

Telephone: (800) 553-6847
Facsimile: (703) 605-6900
E-Mail: orders@ntis.gov
Online order: <http://www.ntis.gov/search>



SAND2016-0521
Unlimited Release
Printed January 20, 2016

Evaluation of Strontium Selectivity by Sandia Octahedral Molecular Sieves (SOMS)

Mark J. Rigali
Applied Systems Analysis and Research Department

Thomas A. Stewart
Geochemistry Department

Sandia National Laboratories
P.O. Box 5800
Albuquerque, New Mexico 87185-MS0747

Abstract

Sandia National Laboratories has collaborated with Pleasanton Ridge Research Company (PRRC) to determine whether Sandia Octahedral Molecular Sieves (SOMS) and modified SOMs materials can be synthesized in large batches and produced in granular form. Sandia National Laboratories tested these SOMs and its variants based in aqueous chemical environments for an application-based evaluation of material performance as a sorbent. Testing focused primarily on determining the distribution coefficients (K_d) and chemical selectivity SOMs for alkali earth (Sr) ions in aqueous and dilute seawater solutions. In general the well-crystallized SOMs materials tested exhibited very high K_d values ($>10^6$) in distilled water but K_d values dropped substantially ($\sim 10^2$ - 10^3) in the dilute seawater (3%). However, one set of SOMs samples (1.4.2 and 1.4.6) provided by PRRC yielded relatively high K_d (approaching 10^4) in dilute seawater. Further examination of these samples by scanning electron microscopy (SEM) revealed the presence of at least two phases at least one of which may be accounting for the improved K_d values in dilute seawater.

CONTENTS

1. INTRODUCTION	7
2. EXPERIMENTAL	8
3. RESULTS AND DISCUSSION	9
4. CONCLUSIONS	14
5. REFERENCES	14

FIGURES

Figure 1. Structure of SOMS.	7
Figure 2. Powder XRD patterns of SMOS samples synthesised by PRRC	9
Figure 3. SEM secondary electron image (left) and backscattered image (right) of 1.5.1 at 250X magnification.	12
Figure 4. SEM secondary electron image of 1.5.1 at 3,230X magnification.	12
Figure 5. SEM secondary electron image (left) and backscattered image (right) of 1.4.2 at 250X magnification.	13
Figure 6. SEM secondary electron image (left) and backscattered image (right) of the rod-like material in 1.4.2 at 1,250X magnification.	13

TABLES

Table 1. Percent Uptake of Sr and K_d s in selected SOMS samples	11
--	----

NOMENCLATURE

DOE	Department of Energy
K_d	Distribution Coefficient
PRRC	Pleasanton Ridge Research Company
SEM	Scanning Electron Microscopy
SNL	Sandia National Laboratories
SOMS	Sandia Octahedral Molecular Sieves
XRD	X-ray Diffraction

1. INTRODUCTION

At Fukushima and several US Department of Energy (DOE) sites, radioactive waste lingers in hundreds of tanks containing a highly radioactive mix of supernate liquid, solid salt cake and sludge. DOE has pledged to clean up these sites by 2025. The waste contains, among others, the radioactive isotopes of cesium and strontium (specifically Cs-137 and Sr-90) that are gamma and beta emitters with high decay energies that contribute to undesirable heat generation. In order to store these wastes long term, Cs-137 and Sr-90 need to be removed. In addition to this national long-term issue, the Fukushima Daichi disaster released both Cs and Sr and other radionuclides to land and sea. Currently, there are millions of gallons of Cs-137 and Sr-90 contaminated water in storage tanks at the Fukushima site. Cs clean-up is underway and Sandia National Laboratories (SNL) developed technology is in use but an effective sorbent media for Sr remediation is still actively being sought by the Japanese.

For the past two decades, Sandia has been developing technologies for radioactive response, decontamination and site remediation/restoration. As a result Sandia has developed and patented a number of highly effective sorbents for radionuclide remediation. Several of these are currently in use at nuclear facilities. For example, the Sandia patented crystalline silico-titanates have been used in the treatment of more than 160 million gallons of Cs contaminated water at Fukushima through a license agreement and development effort with Honeywell UOP. The Sandia-developed Monosodium titanates are being utilized by Harrell Industries Inc. at Savannah River for tank waste remediation.

Sandia Octahedral Molecular Sieves (SOMS) developed and patented by Sandia are a class of niobium framework compounds that have shown excellent selectivity for Sr and other alkali earth metals (Figure 1). This team proposes to demonstrate that patented SOMS are effective for remediating radioactive Sr at Fukushima. While it is expected that SOMS will also be effective for Sr remediation at US DOE sites, as a longer term opportunity given the current timetable for radionuclide remediation at the DOE sites, the ultimate goal of this effort is to develop and license SOMs to industry for Fukushima and DOE site clean-up.

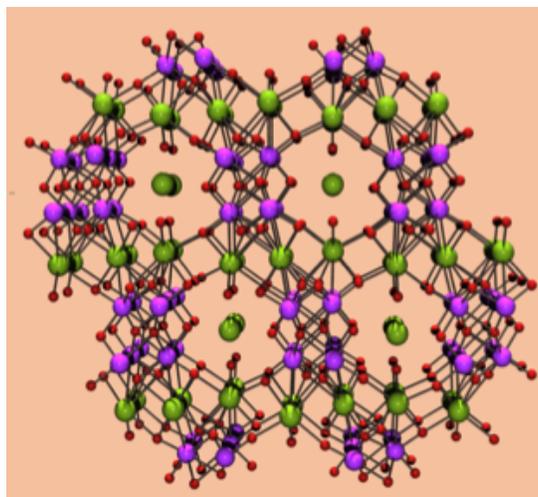


Figure 1. Structure of SOMS.

2. EXPERIMENTAL

SOMS and SOMS variants were synthesized using the oxide route by Pleasanton Ridge Research Company (PRRC). X-ray diffraction (XRD) was used to determine sample purity and verify that the synthesis product was SOMS. PRRC then provided SOMS samples to Sandia for sorption testing.

SOMS selectivity for Sr was measured in distilled water, in the presence of Ca, and in dilute seawater. Solutions were prepared with 10 ppm $\text{Sr}(\text{NO}_3)_2$. Forty-milliliter solutions were combined with 0.04 g of SOMS in 100 mL polypropylene bottles. The mixtures were capped and rocked at 85 rpm at room temperature on an orbital shaker platform for 24 hours. Duplicate mixtures were prepared for each analysis. After contacting the SOMS, solutions were centrifuged, filtered and analyzed for Sr. The Sr analyses were carried out in Sandia's Geochemistry Laboratory using inductively coupled plasma mass spectroscopy.

Percent cation removal reflects Sr uptake by the sample. It is a simple ration of the Sr taken up by the sorbent over the amount of Sr in the starting solution:

$$\% \text{Cation Removal} = (\text{CSC} - \text{CRS}) / \text{CSC} \times 100$$

Distribution coefficients were calculated using the relationship below following the analyses of Nyman et al., 2002.

$$K_d (\text{mL/g}) = ([\text{Srix}]/\text{gix}) / ([\text{Srsln}]/\text{mL sln})$$

where K_d is the distribution coefficient, ix is ion exchanger, $[\text{Srix}]$ is the concentration of Sr adsorbed by the ion exchanger, gix is the weight of the SOMS ion exchanger, $[\text{Srsln}]$ is the concentration of the Sr remaining in solution after contacting SOMS, and mL sln is milliliters of solution.

3. RESULTS AND DISCUSSION

Based on the powder XRD patterns shown in Figure 2 samples 1.4.2 and 1.4.6 were chosen for Sr selectivity experiments from the first lot of samples provided by PRRC because they appeared to exhibit the highest degree of crystallinity and purity. Duplicates were run for each sample and the data presented below are the average values of the two experimental analyses. Measured Sr uptake is significant in both samples (Table 1). Of particular note is that the K_d of Sr in dilute simulated seawater is twice that of the K_d in distilled water for sample 1.4.2.

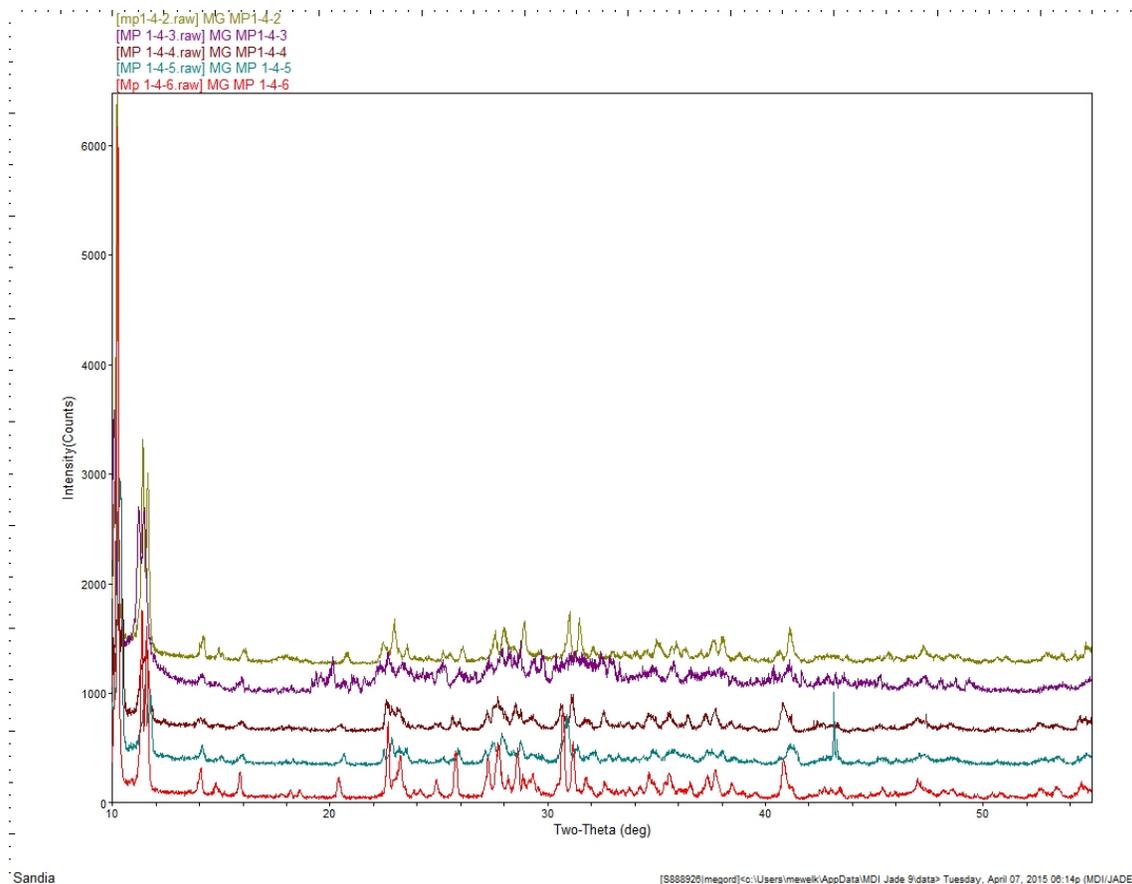


Figure 2. Powder XRD patterns of SOMS samples synthesized by PRRC.

This result is surprising in light of the expectation that the K_d should drop significantly in seawater due to the presence of competing cations such as Ca for the SOMS exchange sites. In addition, Nyman et al., 2002 report K_d values as high as 100,000 or greater for Sr in distilled water. Furthermore a comparison to other samples of well-crystallized SOMS provided by PRRC in the 1.5 and 1.6 lots (Table 1), specifically 1.5.1 and 1.6.2, exhibit the expected high K_d values in distilled water and a significant drop-off in Sr uptake in dilute seawater samples.

Given the results the Sr sorption experiments were rerun on sample 1.4.2 to verify performance. In this experiment extra care was taken to disaggregate the sample powders which were observed to clump when the Sr solution was added to the sample vial. Disaggregation should result in improved Sr uptake because more sample surface area is exposed to the Sr bearing solutions. As

expected, the resulting K_d values showed a $\sim 2x$ improvement in uptake and again the Sr uptake in dilute seawater was higher than that observed in distilled water.

The samples selected from the 1.5 and 1.6 series yielded results typical of SOMS although the sharp drop-off in Sr uptake in dilute seawater was substantial and higher than expected. The Sr selectivity data suggest the possible presence of a second phase or contaminant in 1.4 series of samples that may be involved in Sr uptake. In order to assess the presence of a second phase, samples 1.5.1 and 1.4.2 were examined by scanning electron microscopy (SEM). Sample 1.5.1 shown in Figure 3 and Figure 4 exhibits fairly uniform clusters of needle-like crystals, between 10 and 40 microns in length, with high aspect ratios. The material appears composed of a single phase as indicated by the crystal uniformity (Figure 3 left) and the lack of Z-contrast in the backscattered image (Figure 3, right) It is comparable both morphologically and chemically (as indicated by the K_d data below) to the SOMS materials prepared by Nyman et al., 2002.

Table 1. Percent Uptake of Sr and K_d s in selected SOMS samples

SOMS 1.4.2				
Test Description	Cation starting concentration (CSC) (ppm)	Cation remaining in solution (CRS) (ppm)	Percent Cation Removal	K_d
Sr in DI water	9.74	1.75	64.01	1775
Ca in DI water	11.57	6.1	47.32	897
Sr in 3% seawater	15.69	3.14	79.99	3997
Sr in 10% seawater	18.79	9.87	47.50	904
SOMS 1.4.2 (Rerun)				
Sr in DI water	10.36	2.41	76.74	3299
Ca in DI water	12.32	5.66	54.10	1177
Sr in 3% seawater	15.77	1.68	89.35	8397
Sr in 10% seawater	18.11	11.64	35.75	556
SOMS 1.4.6				
Sr in DI water	10.35	2.62	74.69	2950
Ca in DI water	13.17	7.39	43.89	782
Sr in 3% seawater	NA	NA	NA	NA
Sr in 10% seawater	18.96	10.98	42.64	743
SOMS 1.5.1				
Sr in DI water	9.98	0.085	99.13	116412
Ba in DI Water	7.23	0.34	95.26	20265
Ca in DI water	18.1	3.33	81.60	3945
Sr in 3% seawater	15.2	10.58	30.43	437
Sr in 10% seawater	84.7	74.5	12.04	137
SOMS 1-6-2				
Sr in DI water	11.6	0.09	99.22	127889
Sr in 3% seawater	10.9	5.8	46.79	879
Sr in 10% seawater	ND	ND	ND	ND
SOMS 1-6-5				
Sr in DI water	11.6	0.14	98.79	81857
Sr in 3% seawater	10.9	6.08	44.22	793
Sr in 10% seawater	ND	ND	ND	ND
Pr-8-1a				
Sr in DI water	10.45	10.60	0	1
Sr in 3% seawater	10.25	10.2	0	1
Sr in 10% seawater	ND	ND	ND	ND

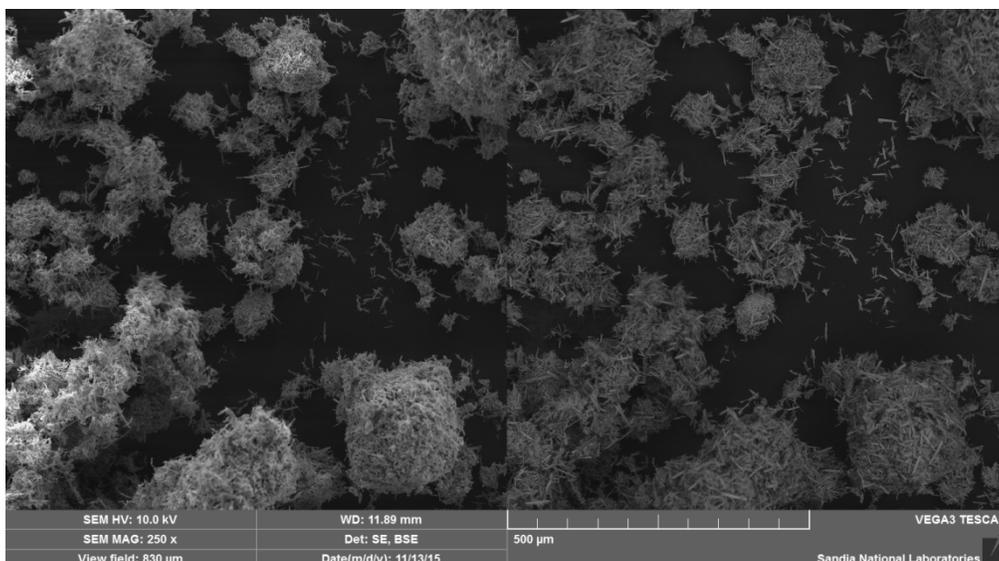


Figure 3. SEM secondary electron image (left) and backscattered image (right) of 1.5.1 at 250X magnification.

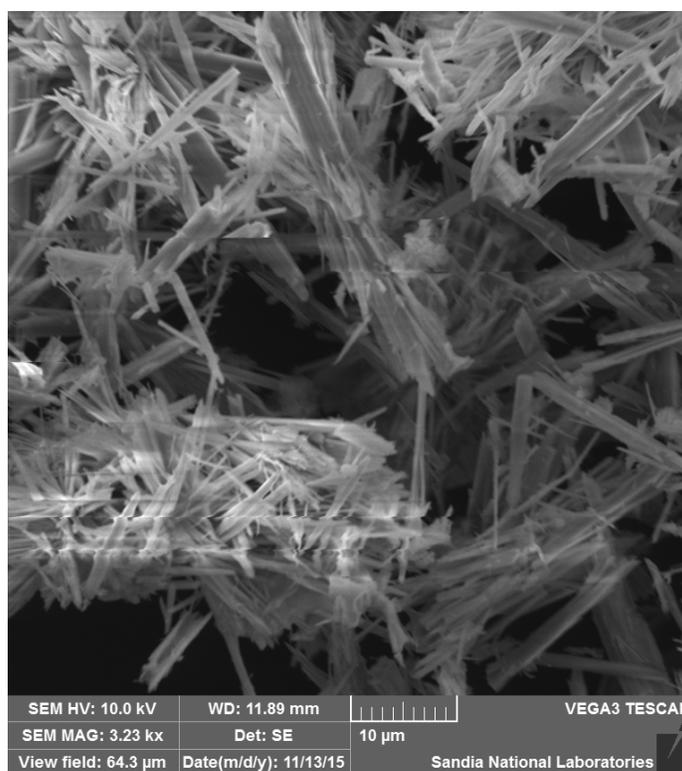


Figure 4. SEM secondary electron image of 1.5.1 at 3,230X magnification.

In contrast, sample 1.4.2 exhibits at least two distinct phases (Figure 5). Clusters of highly irregular, grainy, non-uniform crystals are present along with relatively long rod-like crystals, 200-300 microns in length. Virtually absent are the uniform needle-like crystals seen in sample 1.5.1.

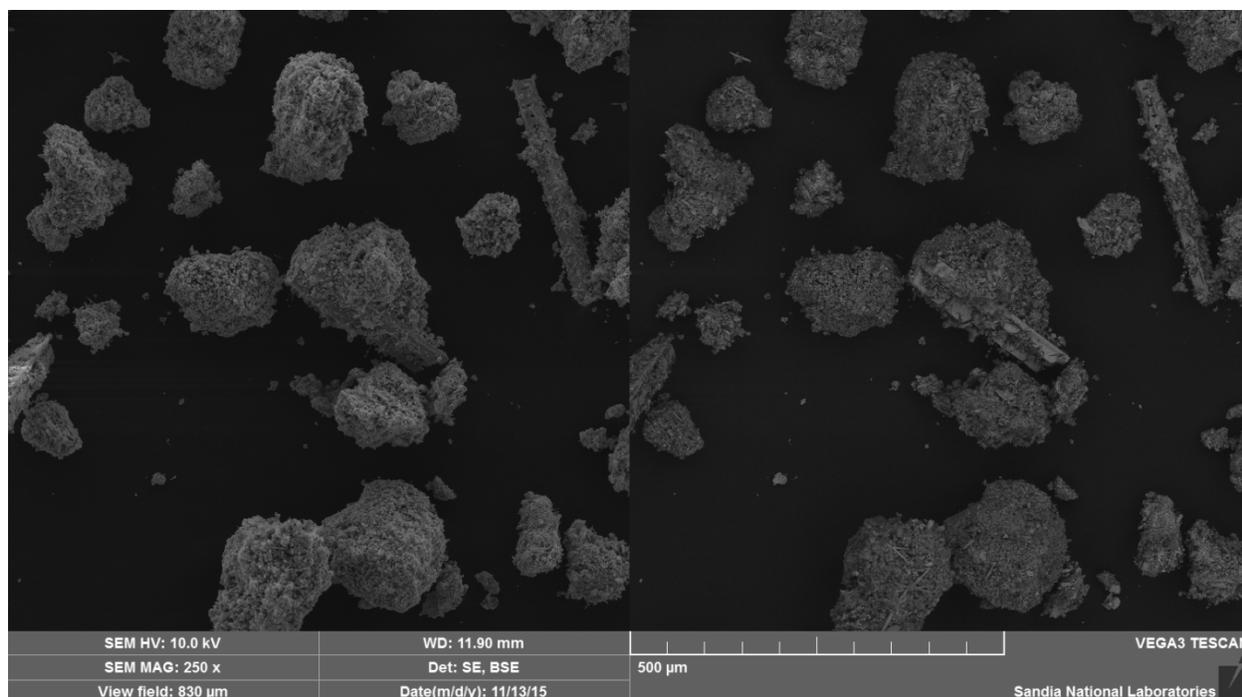


Figure 5. SEM secondary electron image (left) and backscattered image (right) of 1.4.2 at 250X magnification.

A close up image of one of the rod-like structures in Figure 1.4.2 reveals the presence of a few needle-like crystals on the surface of the rod. Note that these needle-like crystals are darker (Figure 6, right) than the rod indicating a distinctly lower Z-contrast and this is consistent with the hypothesis that there are two different chemically distinct phases present. One of these phases may be hexaniobate, a commonly observed precursor to SOMS.

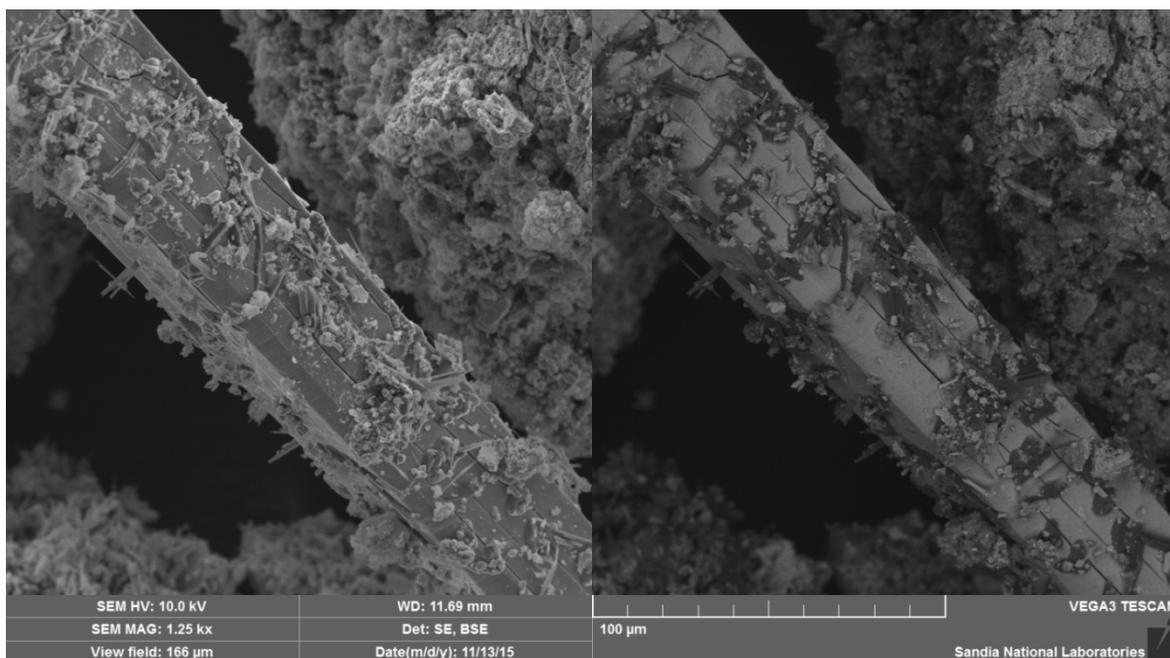


Figure 6. SEM secondary electron image (left) and backscattered image (right) of the rod-like material in 1.4.2 at 1,250X magnification.

4. CONCLUSIONS

The dramatic fall off in K_d values in the presence of dilute seawater suggests that SOMS will not perform well for the removal of Sr from dilute seawater as is the case with the Sr contaminated Fukushima tank water. However, the 1.4 series of samples show better Sr selectivity in dilute seawater as the K_d values of the measured samples approach 10^4 . The 1.4 series of samples appear to be different both morphologically and chemically suggesting the presence of an as yet unidentified phase (or phases) that is contributing to or perhaps controlling Sr selectivity and uptake.

Future work should focus on the following:

- Identification of the phase or phases in the 1.4 series of samples that is influencing Sr selectivity and uptake
- If possible optimize synthesis routes to create a pure phase
- Test Sr uptake and selectivity of the pure phase

5. REFERENCES

1. Nyman, M. D., A. Tripathi, J. B. Parise, R. S. Maxwell, W. T. A. Harrison and T. M. Nenoff. 2001. *A New Family of Octahedral Molecular Sieves*. J. Am. Chem. Soc. 123, p.1529-1530.

Distribution

4 Lawrence Livermore National Laboratory
Attn: N. Dunipace (1)
P.O. Box 808, MS L-795
Livermore, CA 94551-0808

1	MS0734	J. B. Kelley	Org. 6632
1	MS0747	M. J. Rigali	Org. 6224
1	MS0754	T. A. Stewart	Org. 6915
1	MS0899	Technical Library	9536 (electronic copy)

