

Hydrothermal Synthesis and Analysis of Iodine-Containing Sodalite - 16153

Saehwa Chong,¹ Jacob Peterson,^{2,3} Brian Riley,^{1, 3} John McCloy^{1, 4}

¹Materials Science and Engineering Program, Washington State University, Pullman, WA 99164

²School of Chemical Engineering and Bioengineering, Washington State University, Pullman, WA 99164

³Pacific Northwest National Laboratory, Richland, WA 99352

⁴School of Mechanical and Materials Engineering, Washington State University, Pullman, WA 99164

ABSTRACT

Five process variables affecting hydrothermal synthesis of iodide sodalite, $\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{I}_2$, were investigated, including NaOH concentration, aging time, temperature, Al/Si ratio, and precursor concentration. X-ray powder diffraction was performed to characterize synthesized samples, and Rietveld refinement method was used to quantify the mass fractions of phases. Iodide sodalite yield increased, in general, as NaOH concentration, aging time, and temperature increased. Lowering the Al/Si ratio from 1 to 0.5 increased the formation of cancrinite. Diluting the precursor concentration in the mixed solution with water revealed that nepheline hydrate-1, a zeolite, formed rather than sodalite. This observation, along with the preferential formation of zeolite A in samples where no NaOH was added, suggests that mechanisms for transport of the ions and formation of the aluminosilicate frameworks vary with hydrothermal conditions. The model for the best synthesis conditions based on the four significant variables is presented.

INTRODUCTION

The highly volatile radionuclide, I-129, has a long half-life and is difficult to immobilize. Iodine is not easily vitrified by conventional routes due to its volatility at typical glass processing temperatures. Therefore, there have been many efforts to develop an alternative waste form for iodine, but none has been uniquely accepted by the nuclear waste community due to trade-offs regarding loading capacity, chemical durability, processing efficiency, and cost [1-3]. Some prominent approaches to immobilize iodine include the development of AgI containing glasses [4], bismuth-oxyiodide minerals [5], silver functionalized silica aerogels [6], metal-organic frameworks [7], Pb and/or Ag containing vanadinite apatites [8, 9], and sodalite [10-12]. Sodalite, written as $\text{M}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{X}_2$ where M and X typically represent an alkali cation and monovalent anion respectively, has been studied extensively for immobilization of chlorine, and was proposed as the baseline mineral for the spent electrochemical salt waste [13, 14]. However, relatively few studies have been made on sodalite for immobilization of iodine [15-19].

Iodide sodalite is a promising candidate for immobilization of radioactive iodine due to its ability to capture iodine in the β -cage of the sodalite crystal structure. Sodalite, as portrayed in Fig. 1, is composed of aluminosilicate framework forming β -cages with an anion at the center surrounded by cations and has cubic lattice system with $P\bar{4}3n$ [20] or $I\bar{4}3m$ symmetry [21]. However, there are challenges

associated with synthesizing iodine-containing sodalite, particularly for a waste form. Typical solid state processing routes require high temperatures, which might be undesirable due to the high volatility of iodine. One potential solution to this processing challenge is low temperature growth using various simple aqueous-based or hydrothermal (aqueous at higher pressure) synthesis routes.

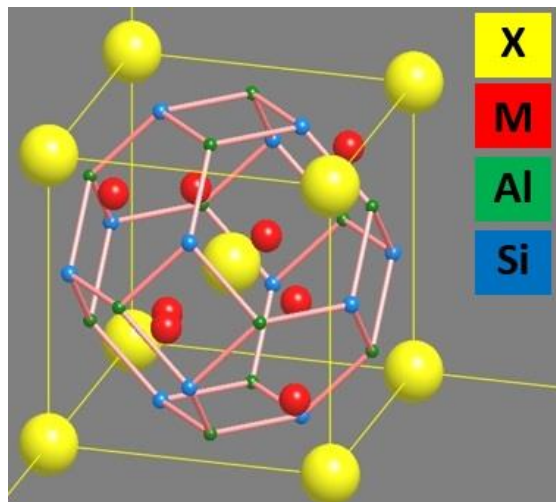


Fig. 1. Sodalite structure where X and M represent an anion and a cation, respectively.

Our current work is focused on the hydrothermal synthesis of iodide-containing sodalite. Hydrothermal synthesis is a one-step growth method at relatively low temperature ($< 200^{\circ}\text{C}$) in a sealed vessel with water, resulting in above atmospheric pressure inside the vessel. One potential challenge with hydrothermal synthesis of iodide sodalite is competition of the hydroxide anion for iodide in the β -cage, since syntheses are typically performed at high pH using alkali hydroxide, for instance. Additionally, most studies on the hydrothermal synthesis of sodalite use excess halide reagent to avoid OH^- in the β -cage, but this is probably not realistic for a radioactive waste form process where a highly alkaline scrubber solution might be the waste stream.

In this article, we briefly report the synthesis and characterization of iodide sodalite produced without using excessive halide reagents, thus representing a more realistic waste-processing scenario. Our study shows the effects of various process variables (NaOH concentration, aging time, temperature, Al/Si ratio, and precursor concentration) and precursors (zeolite 4A, kaolinite, and sodium aluminate, colloidal silica) on the phase development and phase fraction of crystalline species. In all cases, the iodine was provided by NaI salt. This simple low-temperature synthesis approach has promising practical applications for immobilizing I-129. Our synthesized minerals were characterized by X-ray powder diffraction (XRD) for their atomic structure estimate of iodine waste loading.

EXPERIMENTAL METHODS

Sodium iodide (NaI certified grade, Fisher), sodium aluminate (NaAlO_2 99.9%-Al, Stream Chemicals), colloidal silica (SiO_2 , Sigma Aldrich), and sodium hydroxide (NaOH certified ACS grade, Fisher) were used as-received for variable-effect experiments, such as temperature, aging time, and water content. The

stoichiometric ratio of NaI:NaAlO₂:SiO₂ was 1:3:3, by mole, for iodide sodalite synthesis. In general, approximately 0.500 g of NaI, 0.823 g of NaAlO₂, and 0.601 g of SiO₂ were mixed in 11.25 mL of deionized water (DIW).

One-variable-at-a-time experiments were conducted to investigate each effect as summarized in Table I. For the NaOH concentration variation study, a different amount of NaOH was mixed with addition of 3.75 mL of DIW to the initial 11.25 mL solution. In other words, 4 M, 8 M, and 11 M in Table I mean adding 3.75 mL of those NaOH concentrations, and the mixed solutions have NaOH concentration of 1 M, 2 M, and 2.75 M respectively. Roughly 15 mL of the mixed solution was put in an autoclave (Parr 200 mL acid digestion vessel) and placed in an oven at 180°C for 2 d. For the aging time variation study, samples were in an oven at 100°C for 1–20 d. Two sets of samples with either 0 or 11 M NaOH concentration were synthesized. For the temperature variation study, three samples were synthesized at 100°C, 140°C, or 180°C, covering the typical hydrothermal process temperature range for sodalite minerals [22-25]. For the Al/Si ratio study, an excess amount NaAlO₂ or SiO₂ was added to the initial stoichiometric solution to make the Al/Si ratio equal to 1.5 or 0.5. Therefore, for Al/Si ratio equal to 1.5, it is not just excess Al but also Na. For the precursor concentration study, a dilution was performed by adding 15 mL or 30 mL of extra DIW to the previously mixed solutions. The diluted solution was heated at 180°C for 2 d. After processing, all the synthesized samples were washed 3 times for 5 min each using a centrifuge at 9000 rpm then subsequently dried at 90°C overnight.

XRD and Rietveld analysis were performed on synthesized samples. XRD spectra were obtained using a PANalytical X'Pert Pro MPD (The Netherlands). Scans were performed with a Cu-K α X-ray source at 45 keV and 40 mA in the range of 10-90° 2 θ with 0.002° 2 θ step and 11-s dwell. For Rietveld analysis, samples were doped with 10 mass% NIST SRM-674b (ZnO) as an internal standard to quantify phases and crystalline fraction, and subsequently analyzed using Highscore software (PANalytical).

TABLE I. One-variable-at-a-time synthesis conditions

Variable Experiment	Precursor ratio	Added NaOH concentration (M)*	Aging time (d)	Temperature (°C)	Al/Si ratio	Extra water added (mL)
NaOH variation	conc. stoichiometric	0, 4, 8, 11	2	180	1	0
Aging variation	time stoichiometric	11	1, 5, 10, 20	100	1	0
Aging variation	time stoichiometric	0	1, 5, 10, 20	100	1	0
Temperature variation	stoichiometric	11	2	100, 140, 180	1	0
Adjusting ratio	Al/Si not stoichiometric	11	2	180	0.5, 1, 1.5	0
Precursor concentration	stoichiometric	11	2	180	1	0,15,30

* 3.75 mL of X M NaOH is added where X=4, 8, or 11.

RESULTS

NaOH Concentration Variation Study

The effect of NaOH concentration on product yield was investigated by adding 3.75 mL of different NaOH concentration solution to 11.25 mL of stoichiometric solution. XRD patterns and phase mass percentages are shown in Fig. 2. As NaOH concentration increased, more iodide sodalite was formed, and overall crystalline fraction increased. Also, it can be seen that major peaks of analcime 1C phase ($\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$) at $25.9^\circ(2\theta)$ and hydrosodalite phase $[\text{Na}_8(\text{AlSiO}_4)_6 2(\text{H}_2\text{O})(\text{OH})_2]$ at $14^\circ(2\theta)$ decreased as the NaOH concentration increased. It should be noted that iodide sodalite and hydrosodalite have several similar peak positions such as near 14° and 24° , which were taken into account during refinement. However, it can be seen that higher NaOH concentration favored iodide sodalite formation as a decrease in the intensity of the peak at $14^\circ(2\theta)$ mainly reflects the decrease in hydrosodalite yield.

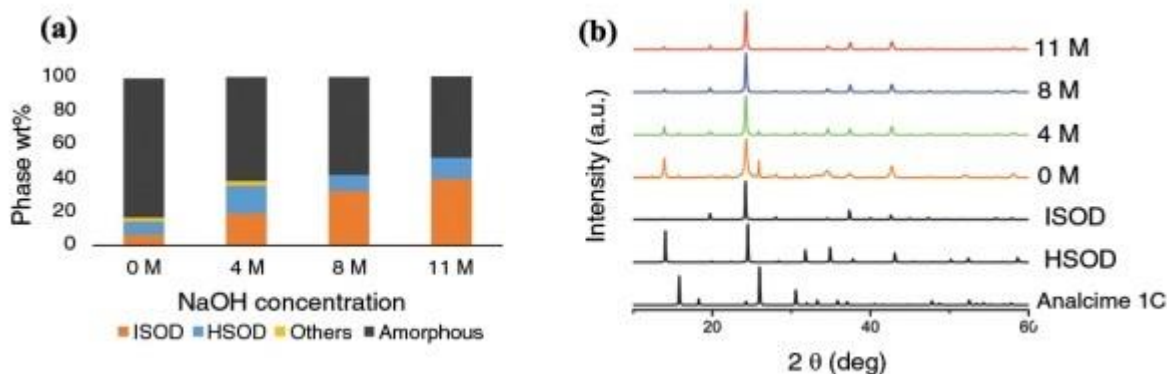


Fig. 2. (a) Phase wt% distribution for different NaOH concentration. ISOD and HSOD denote iodide sodalite and hydrosodalite respectively. (b) Normalized XRD patterns of synthesized minerals and reference phases (ISOD ICSD# 41193, HSOD ICSD# 413496, and analcime 1C ICSD#15811)

Aging Time Variation

The study of the effect of aging time involved 2 sets of samples, one with and one without added NaOH. The mixed solutions were aged at 100°C for 1, 5, 10, or 20 d. Longer aging time resulted in higher iodide sodalite yield as shown in Fig. 3. For 20 d of aging with 11 M NaOH, the synthesized mineral was almost pure iodide sodalite, but about half of the sample was amorphous based on Rietveld analysis. Synthesized minerals without NaOH were mainly zeolite A and zeolite P1, and almost no sodalite phase was present regardless of aging times. Zeolite A formation at 90°C was observed in other studies when NaOH concentration was low [22], thus it is not surprising that zeolite A was observed at 100°C in experiments without added NaOH. The transformation of zeolite to sodalite can be seen between the 1-d and 5-d samples, and this zeolite-sodalite phase transformation was observed in other studies [22]. It should be noted that the colloidal SiO_2 precursor does contain some NaOH in the liquid containing the colloidal particles, and the pH of this solution was 9.0.

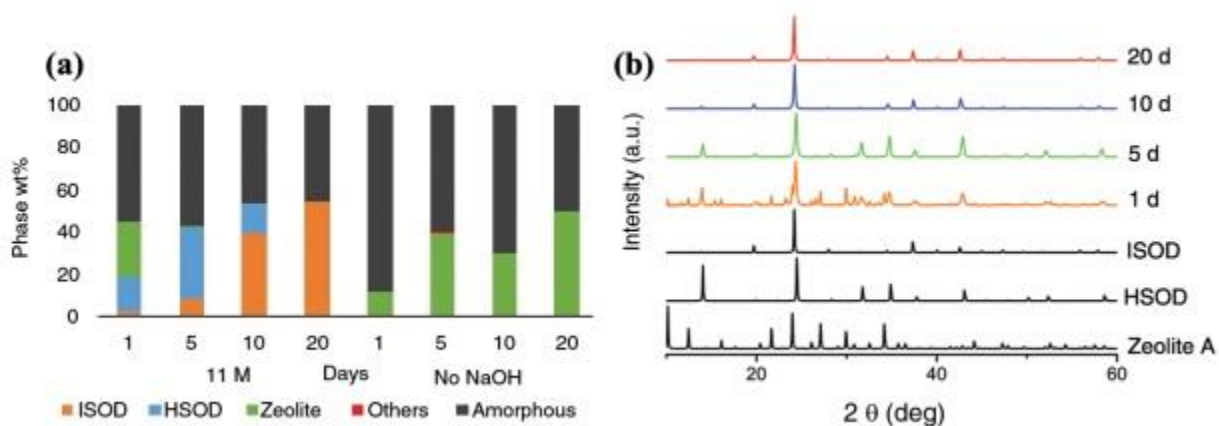


Fig. 3. (a) Phase wt% for aging time variation on 11 M and no NaOH samples. **(b)** Normalized XRD patterns of 11 M NaOH samples and reference phases (zeolite A ICSD# 183702).

Temperature Variation

The temperature variation study consisted of samples produced at 100°C, 140°C, and 180°C with 11 M NaOH and 2 d aging time. Higher temperature generally resulted in higher iodide sodalite yield (Fig. 4). The 140°C sample showed the highest yield, but it was very similar to that of 180°C. Lower processing temperatures favored formation of hydrosodalite. Crystalline fractions were similar for all 3 temperatures.

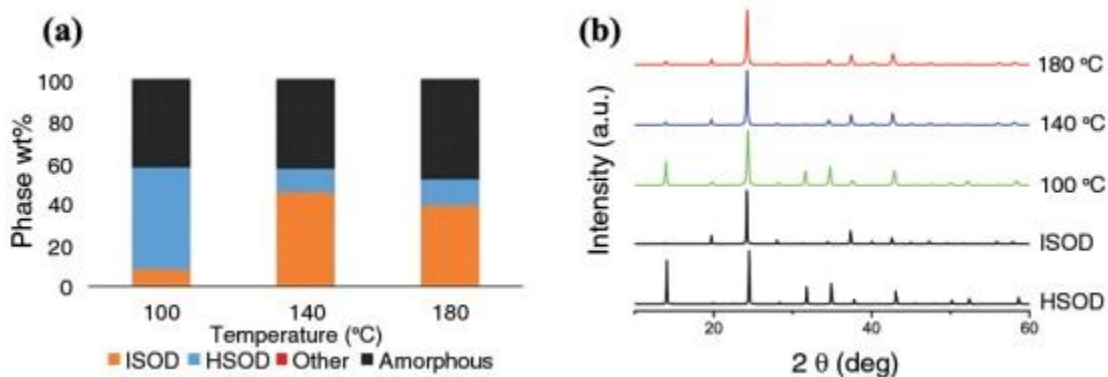


Figure. 4. (a) Phase wt% for temperature variation. **(b)** Normalized XRD patterns of synthesized mineral and reference phases.

Adjusting Al/Si Ratio

The effect of the Al/Si ratio on the product was investigated by adding excess NaAlO₂ or SiO₂ to initial stoichiometric solution to make the Al/Si ratio equal to 1.5 or 0.5. Excess Na and Al favored the formation of hydrosodalite, whereas the excess Si favored the formation of the cancrinite, Na_{7.34}(AlSiO₄)₆(OH)_{1.68}(H₂O)_{7.56}, as shown in Fig. 5. Crystalline fractions changed minimally among the different Al/Si ratios.

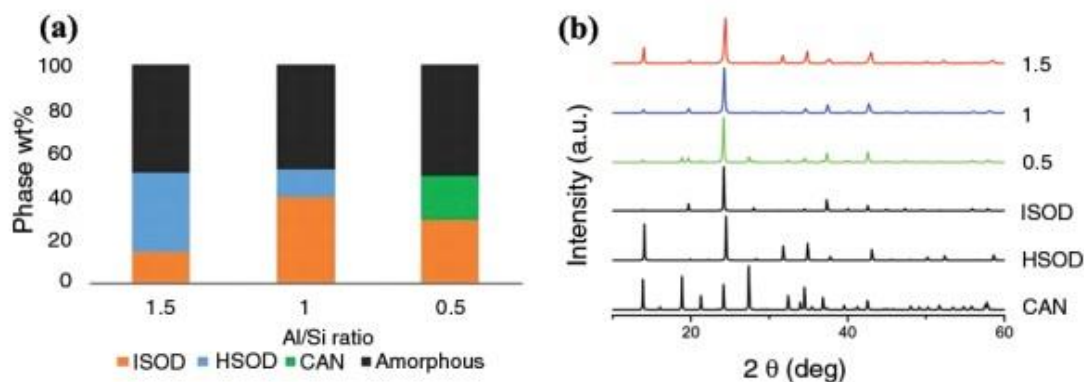


Figure. 5. (a) Phase wt% for different Al/Si ratio. (b) Normalized XRD patterns of synthesized samples and reference phases; CAN denotes cancrinite (CAN ICSD# 411486).

Precursor Concentration

The effect of precursor concentration variation was investigated by adding extra DIW to the initial stoichiometric solution. Three samples were synthesized at 180°C with the total amounts of DIW equal to ~15 mL, 30 mL, or 45 mL. Lowering precursor concentration favored the formation of hydrosodalite and nepheline hydrate 1, $\text{Na}_3(\text{Al}_3\text{Si}_3\text{O}_{12})(\text{H}_2\text{O})$, a "JBW" framework zeolite [26, 27]. This result is consistent with other studies where lowering NaOH concentration favored nepheline hydrate 1 formation over sodalite at 200°C [27]. Although the current work involved lowering all precursor concentrations including NaOH, the effect should be relevant when lowering NaOH concentration alone. Also, it should be noted that with similar conditions but at a lower temperature around 100°C, lowering precursor or NaOH concentration favored the formation of zeolite A.

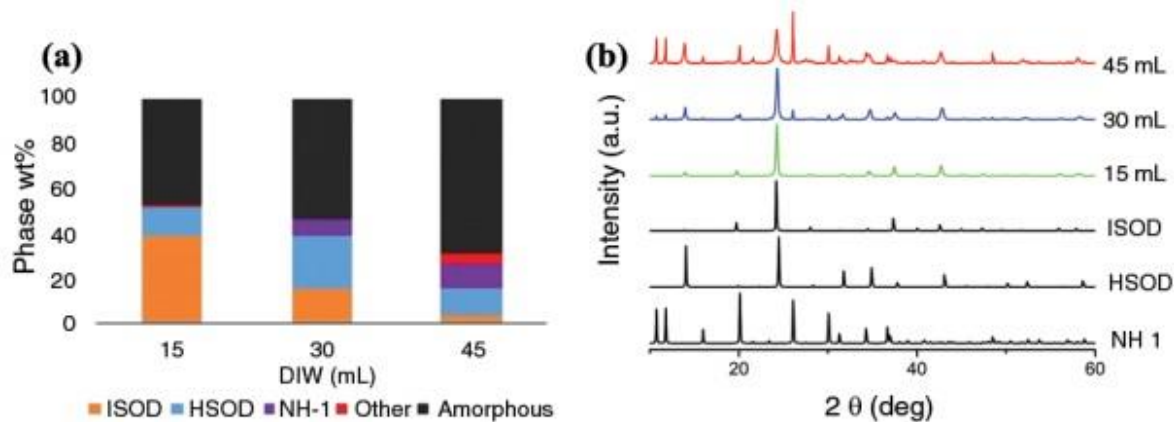


Fig. 6. (a) Phase wt% for precursor concentration variation. NH 1 denotes nepheline hydrate 1. (b) Normalized XRD patterns of synthesized samples and reference phases (NH 1 ICSD# 17069)

Model for Optimal Synthesis Condition

Using all the data of one-variable-at-a-time variation experiments with JMP software (version 11, SAS), the model for optimal synthesis condition to maximize iodide sodalite yield was designed. All the variables were input as continuous

variables. Among the five process variables, Al/Si ratio was not used because it was determined to be less significant according to the software algorithm. The model predicted optimal conditions for maximum iodide sodalite yield was at 11 M NaOH concentration, 20-d aging time, 155°C processing temperature, and without dilution. The interaction profile diagram at the optimal condition is shown in Fig. 7.

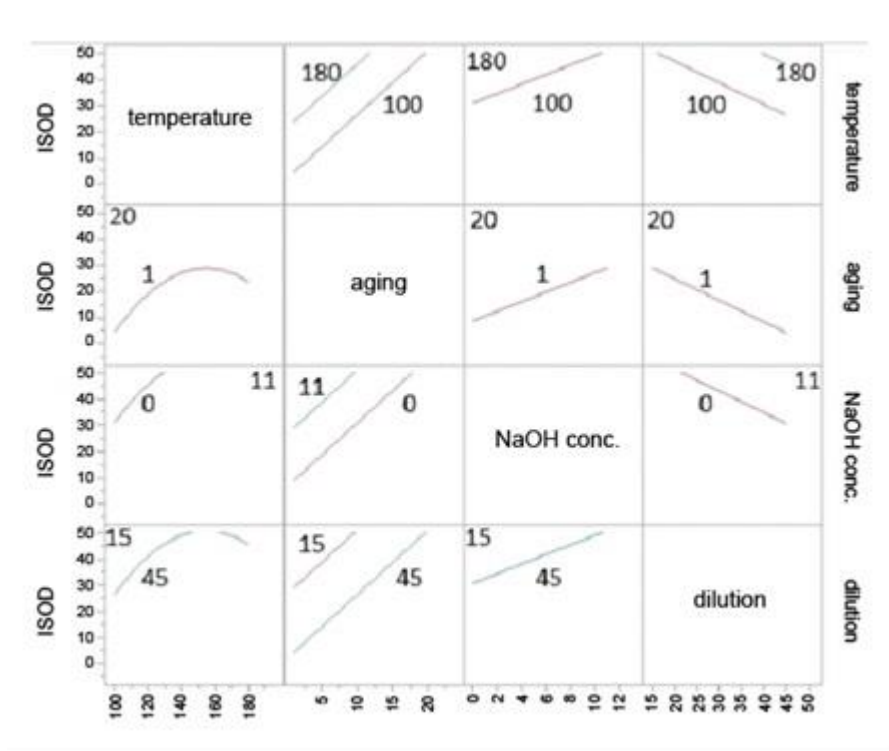


Fig. 7. Interaction profile diagram for the optimal hydrothermal condition when using NaAlO_2 , SiO_2 , NaI , and NaOH within given experiment ranges.

CONCLUSIONS

Five process variables were investigated to determine their relationship to iodide sodalite formation. Increased in NaOH concentration, temperature, and aging time, in general, resulted in higher iodide sodalite yield. Excess Si/Al favored cancrinite formation whereas excess sodium and aluminum favored hydrosodalite formation. Lowering precursor concentration yielded the nepheline hydrate 1 phase at the 180°C synthesis temperature. The synthesis without NaOH at 100°C favored zeolite A formation. The formation of zeolite A before sodalite in the aging experiments suggests that zeolite A is a precursor phase. High NaOH concentration, longer aging time, and higher precursor concentration produced higher overall crystalline fraction (lower amorphous content). By contrast, temperature and Al/Si affected the crystalline phase distribution but not so much the overall crystal fraction within the tested range. A model for optimal conditions for iodide sodalite was designed, and it agreed with the general trends seen in one-at-a-time variation experiments. This model can be helpful for hydrothermal synthesis when using NaAlO_2 , SiO_2 , and NaI precursors with NaOH .

REFERENCES

- 1 L.L. BURGER, R.D. SCHEELE, and K.D. WIEMERS, "Selection of a form for fixation of iodine-129," PNL-4045, Pacific Northwest Laboratory, Richland, WA (1981).
- 2 P. TAYLOR, "A review of methods for immobilizing iodine-129 arising from a nuclear fuel recycle plant, with emphasis on waste-form chemistry," AECL-10163, Whiteshell Nuclear Research Establishment, Pinawa, Manitoba, Canada (1990).
- 3 M.I. OJOVAN and W.E. LEE, *An Introduction to Nuclear Waste Immobilisation*. Elsevier Science, Amsterdam (2005).
- 4 T.J. GARINO, T.M. NENOFF, J.L. KRUMHANS�, and D.X. RADEMACHER, "Low-Temperature Sintering Bi-Si-Zn-Oxide Glasses for Use in Either Glass Composite Materials or Core/Shell 129I Waste Forms," *Journal of the American Ceramic Society*, 94(8), 2412-2419 (2011).
- 5 J.L. KRUMHANS� and T.M. NENOFF, "Hydrotalcite-like layered bismuth-iodine-oxides as waste forms," *Applied Geochemistry*, 26(1), 57-64 (2011).
- 6 J. MATYÁŠ and R. ENGLER, "Assessment of Methods to Consolidate Iodine-Loaded Silver-Functionalized Silica Aerogel," *Pacific Northwest National Laboratory, PNNL-22874*, (2013).
- 7 B. ASSFOUR, T. ASSAAD, and A. ODEH, "In silico screening of metal organic framework for iodine capture and storage," *Chemical Physics Letters*, 610, 45-49 (2014).
- 8 F. AUDUBERT and J. LARTIGUE, "Iodine immobilization in apatites," Proc. 4 Atalante Conference (2000).
- 9 F. AUDUBERT, J. CARPENA, J. LACOUT, and F. TETARD, "Elaboration of an iodine-bearing apatite Iodine diffusion into a Pb₃(VO₄)₂ matrix," *Solid State Ionics*, 95(1), 113-119 (1997).
- 10 T. NAKAZAWA, H. KATO, K. OKADA, S. UETA, and M. MIHARA, "Iodine immobilization by sodalite waste form," Proc. Cambridge Univ Press 663 MRS Proceedings, 51 (2000).
- 11 I. BARDEZ, L. CAMPAYO, D. RIGAUD, M. CHARTIER, and A. CALVET, "Investigation of sodalites for conditioning halide salts (NaCl and NaI): Comparison of two synthesis routes," Proc. ATALANTE 2008, O4_19 (2008).
- 12 E. MADDRELL, A. GANDY, and M. STENNETT, "The durability of iodide sodalite," *Journal of Nuclear Materials*, 449(1-3), 168-172 (2014).
- 13 W.L. EBERT, "Testing to Evaluate the Suitability of Waste Forms Developed for Electrometallurgically Treated Spent Sodium-Bonded Nuclear Fuel for Disposal in the Yucca Mountain Repository," ANL-05/43, Argonne National Laboratory, Argonne, Illinois (2005).
- 14 K. BATEMAN, C. KNIGHT, and C. SOLBRIG, "Current Status of Ceramic Waste Form Development," INL/INT-06-11736, (2007).
- 15 E.R. MADDRELL and P.K. ABRAITIS, "A comparison of wastefoms and processes for the immobilization of iodine-129," *Mater. Res. Soc. Symp. Proc.*, 807(Scientific Basis for Nuclear Waste Management XXVII), 261-266 (2004).
- 16 T. NAKAZAWA, H. KATO, K. OKADA, S. UETA, and M. MIHARA, "Iodine immobilization by sodalite waste form," *Mater. Res. Soc. Symp. Proc.*, 663(Scientific Basis for Nuclear Waste Management XXIV), 51-57 (2001).

- 17 W.I. WINTERS, "The Effect of Hot-Pressing Conditions on the Properties of Iodide Sodalite," RHO-LD-153, Rockwell International-Rockwell Hanford Operations, Richland, WA (1980).
- 18 D. STRACHAN and H. BABAD, "Iodide and Iodate Sodalites for the Long-Term Storage of Iodine-129," RHO-SA-83, Rockwell International-Rockwell Hanford Operations, Richland, WA (1979).
- 19 D. HIRABAYASHI, Y. TANADA, T. SUGIYAMA, Y. ENOKIDA, and K. SAWADA, "Low-temperature conversion of spent adsorbent to iodine sodalite by a mechanochemical route," *AIChE J.*, 58(8), 2441-2447 (2012).
- 20 N.C. NIELSEN, H. BILDSØE, H.J. JAKOBSEN, and P. NORBY, "⁷Li, ²³Na, and ²⁷Al quadrupolar interactions in some aluminosilicate sodalites from MAS NMR spectra of satellite transitions," *Zeolites*, 11(6), 622-632 (1991).
- 21 B. BEAGLEY, C. HENDERSON, and D. TAYLOR, "The crystal structures of aluminosilicate-sodalites: X-ray diffraction studies and computer modelling," *Mineralogical Magazine*, 46(341), 459-464 (1982).
- 22 Q. LIU and A. NAVROTSKY, "Synthesis of nitrate sodalite: An in situ scanning calorimetric study," *Geochimica et cosmochimica acta*, 71(8), 2072-2078 (2007).
- 23 M.E. BRENCHLEY and M.T. WELLER, "Synthesis and structures of M₈[AlSiO₄]₆·(XO₄)₂, M= Na, Li, K; X= Cl, Mn Sodalites," *Zeolites*, 14(8), 682-686 (1994).
- 24 C. RIOS REYES, C. DENVER WILLIAMS, and C. ROBERTS, "Synthesis and Characterisation of SOD-, CAN-AND JBW-Type Structures by Hydrothermal Reaction of Kaolinite at 200°C," *Dyna*, 78(166), 38-47 (2011).
- 25 H. TRILL, H. ECKERT, and V.I. SRDANOV, "Mixed Halide Sodalite Solid Solution Systems. Hydrothermal Synthesis and Structural Characterization by Solid State NMR," *The Journal of Physical Chemistry B*, 107(34), 8779-8788 (2003).
- 26 S. HANSEN and L. FÄLTH, "X-ray study of the nepheline hydrate I structure," *Zeolites*, 2(3), 162-166 (1982).
- 27 T. HOFIS and J.-C. BUHL, "Synthesis, hydrothermal stability and thermal reaction behavior of nepheline hydrate I (NH I)," *Reaction Kinetics and Catalysis Letters*, 84(2), 375-382 (2005).

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