

Radioactive wastes

#Kotelnikov A.R., Tikhomirova V.I.,
Gurbanov A.A., Chichagov A.V.
Ushakovskaya T.V., Kovalsky A.M. Synthesis
and study of Mo- and W- bearing sodalites

Institute of Experimental Mineralogy of Russian Academy of
Sciences, Chernogolovka, Moscow distr., 142432

key words: [sodalites, solid solutions, experimental
study]

Introduction. Creation of matrix materials for radionuclides immobilization on the basis of mineral solid solutions is an actual task of experimental mineralogy. For the first time the opportunity of application of sodalites as matrixes for fixing elements of radioactive waste was shown by Pentinghaus et al. [1]. Then the synthesis iodine-bearing sodalite ceramics was carried out in work [2]. The study of leaching resistance has shown high stability of sodalite solid solutions and opportunity of their use as matrix materials. The purpose of the present work was to study molybdenum and tungsten incorporation in sodalites and the possibility of creation of matrixes on the basis of Mo- and W- bearing sodalites.

Synthesis of Mo- and W- bearing sodalites

Starting materials. For the synthesis of Mo- and W- containing sodalites and their solid solutions gels of nepheline ($\text{NaAlSi}_3\text{O}_8$) were used. Natural chlorine containing sodalite (2-4 mg on 100-150 mg gel mixture) were added to starting material. For solution preparation in experiments the distilled water and following salts of high purity ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$) were used.

Run procedure and analytical techniques. The experiences were carried out in the welded platinum tubes (5mm in diameter and 600 mm³ volume). Starting materials (gel mixtures, salts and distilled water) were loaded into the tubes. The concentration of starting solution was 40-60wt.%. Tubes were put into cold seal hydrothermal vessels with external heating. The impermeability of the tubes before and after runs was controlled by weighing.

The experiments were carried out at 450-800°C and $P_{\text{H}_2\text{O}}=1-2$ kbar. The accuracy of temperature controle was

This study was supported by the RFBR grant (project 00-05-64680).

not worse than 5°C and pressure - 50 bars. The duration of experiences was 10-35 days.

The unit cell parameters were refined for all synthesized sodalites. Samples were recorded in the continuous scan mode of the full X-ray diffraction profile on a PC/HZG-4 automated diffractometer. Angular positions of reflections were estimated by the Spectr-8 program (A.V.Okhulkov, IEM RAS) with correction by the internal standard (spectrally pure Si, $a=5.4305$ Å). Unit cell parameters were refined by 12-17 reflections in the angular range of 7-39 degrees (θ) by the LCC, PUDI [3, 4], REFLAT [5] programs. The chemical compositions of solid products were analysed by the "Camebax" microprobe with energydispersive detector Link AN-10000. The ZAF- correction procedure was used for the calculation of the solid solutions compositions. The accuracy of microprobe analysis was not worse than 2.5 mol.%. The DTA study was carried out for a number of synthesized samples.

Results of experiments. The molybdenum and tungsten- containing sodalites and their solid solutions were synthesized in the hydrothermal conditions at 450-800°C and $P_{\text{H}_2\text{O}}=1-2$ kbar. The run conditions and the results of X-ray study are given in Table 1.

The DTA study shows that there is a weight loss (in sodalites synthesized at 450°C) during heating which terminates at 185°C. This effect is connected with the loss of water (1.6 wt.%) evidently. The structural transformation connected to allocation of heat exists above 720°C. As it is seen from data of Table 1 the unit cell parameters of Mo- containing sodalites synthesized at low temperature are a little bit higher than for ones synthesized at high temperatures. This effect is likely connected with incorporation of water in sodalite structure. There is no weight loss during heating the sodalites synthesized at 800°C as it is shown by DTA study. It confirms the absence of water in these sodalites.

The solid solutions of (Mo,W)- bearing sodalites are synthesized under hydrothermal conditions at 800°C and $P_{\text{H}_2\text{O}}=2$ kbar. The synthesized samples are characterized by high crystallinity and their compositions are close to stoichiometric formula. The crystallochemical formula of the synthesized solid solutions of the (Mo,W)- bearing sodalites and the refined unit cell parameters are presented in Table 2.

Table 1. Conditions of synthesis and unit cells parameters of Mo and W- containing sodalites.

Run no.	Phase	T, °C	P, kbar	Run duration, days	a, [Å]	V, [Å] ³
4899	Mo- Sod	450	1	35	9.142(1) ¹⁾	764.0(1)
5001	Mo- Sod	450	1	16	9.142(1)	764.1(1)
4921	Mo- Sod	700	2	11	9.140(1)	763.4(1)
5022	Mo- Sod	800	2	10	9.137(1)	762.8(1)
5121	Mo- Sod	800	2	10	9.137(1)	762.9(1)
5125	W- Sod	800	2	10	9.148(1)	765.7(1)
-	Mo- Sod ²⁾	-	-	-	9.125	759.5
-	W- Sod ²⁾	-	-	-	9.132	761.6

1) standard errors are given in parentheses and refer to the last decimal place; 2) the PDF-2 data.

Table 2. The crystallochemical formula and unit cell parameters of the of the (Mo,W)- bearing sodalite solid solutions synthesized from gel mixtures at 800°C and $P_{H_2O}=2$ kbar.

Run no.	Crystallochemical formula (calculation to 28 oxygen atoms)	$X_W^{Sod\ 1)}$	a, [Å]	V, [Å] ³
5121	$Na_{7.71}[Al_{5.98}Si_{6.14}]_{12.12}(MoO_4)_{0.97}O_{24.12}$	0	9.137(1) ²⁾	762.9(1)
5122	$Na_{8.02}[Al_{5.96}Si_{6.16}]_{12.12}(Mo_{0.73}W_{0.18}O_{3.64})O_{24.36}$	0.21	9.140(1)	763.7(1)
5123	$Na_{8.03}[Al_{5.89}Si_{6.14}]_{12.03}(Mo_{0.53}W_{0.39}O_{3.84})O_{24.16}$	0.40	9.142(1)	764.1(1)
5124	$Na_{7.95}[Al_{6.00}Si_{6.11}]_{12.11}(Mo_{0.24}W_{0.62}O_{3.72})O_{24.28}$	0.72	9.143(1)	764.3(1)
5125	$Na_{8.24}[Al_{5.96}Si_{6.10}]_{12.06}(WO_4)_{0.97}O_{24.36}$	1.00	9.148(1)	765.7(1)

1) mole fraction of W in sodalite solid solution; 2) standard errors are given in parentheses and refer to the last decimal place.

Concentration dependences of unit cell parameters of the (Mo,W)- bearing sodalite solid solutions are approximated by the following equations:

$$a = 9.1369 + 0.024136 * X - 0.0428783 * X^2 + 0.0297945 * X^3 \text{ [Å]} (\pm 0.001), (1)$$

$$V = 762.9 + 6.5134 * X - 12.7779 * X^2 + 9.074614 * X^3 \text{ [Å]}^3 (\pm 0.1), (2)$$

where X - mole fraction of W in (Mo,W)- sodalite solid solution.

The parameters of Margules model (W1 and W2) for the description of excess volume of (Mo,W)- bearing sodalite solid solutions are -4.38(17) cm³/mol and 2.19(9) cm³/mol accordingly. Excess volume is described by the equation:

$$V^c = X * (1 - X) * [-4.38 * X + 2.19 * (1 - X)] \text{ (cm}^3\text{/mol)}, (3), \text{ where X - mole fraction of W in (Mo,W)- sodalite solid solution.}$$

References:

1. Pentinghaus H., Bernotat W., Goettlicher J. Neue Glieder der Sodalith-Strukturfamilie: $SE_4Al_8Si_4O_{24}(MoO_4)_2$. Ergebnisbericht über Forschungs- und Entwicklungsarbeiten 1990, Kfk, Karlsruhe, 1990, pp.12-13.
2. Suvorova V.A., Akhmedzhanova G.M., Zyryanov V.N., Kotelnikov A.R., and Tikhomirova V.I. Study of possible combining radioactive iodine by ceramic matrices based on NaX zeolite. Experiment in Geoscience, 1996, v.5, № 2, pp.50-52.
3. Burnham C.W. IBM computer program for least-squares refinement of crystallographic lattice constants. Geophys. Lab. Carnegie Inst. Washington, D.C., Yearbook, 1962, v.61, pp.132-135.
4. Burnham C.W. Least-squares refinement of crystallographic lattice parameters for IBM PC/XT/AT and compatibles, Harvard University, Cambridge MA02138, 1991 (program description, 24p.)
5. Chichagov A.V. Information-calculating system on crystal structure data of minerals (MINCRYST). Materials Science Forum, vols 166-169, Trans. Tech. Publications, Switzerland, 1994, pp.187-192.

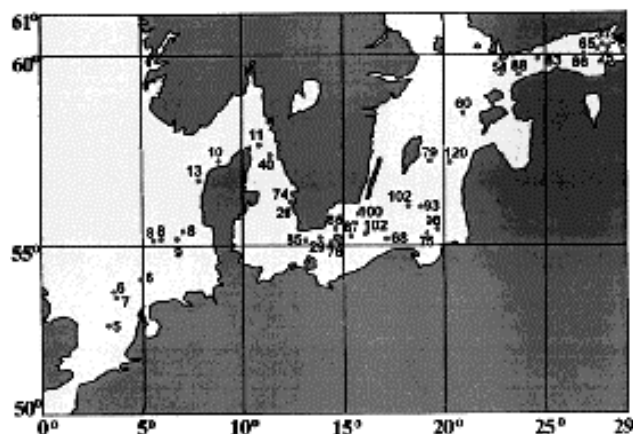
Stepanets O.V.¹, Komarevskii V.M.¹, Borisov A.P.¹, Spiridonov M.A.² Some aspects of ecological and geochemical studies of the Baltic Sea.

1 V.I. Vernadskii's Institute of Geochemistry and Analytical Chemistry, Russian Academy of Science

²A.P. Karpinskii's All-Russian Scientific Geological Institute, Ministry of Natural Resources of the Russian Federation.

Among ecological problems of the Baltic Sea, two are the most serious. The first problem is related to significant pollution of the sea caused by the Chernobyl nuclear power plant accident in 1986, the second is connected with possible depressurization of chemical weapon sunk in 1946 – 47 years and input of poison compounds into environment.

The report presents results of ecological studies in the Baltic Sea performed in 1996 and 1997 years on the scientific ship "Academician Boris Petrov" of the Institute of Geochemistry and Analytical Chemistry, Russian Academy of Science.



Parameters of technogenic pollution in a surface layer of sea water within all studied sea area, as well as in water and bottom sediments in local areas, in places of chemical weapon storage, are exemplified by 40 stations located in the Baltic Sea and south-eastern part of the North Sea.

Data of radiochemical studies indicate, that horizontal distribution of Cs-137 is characterized by spatial fluctuations, whose presence is assigned firstly by irregular input of radionuclides in 1986 year into different parts of the Baltic Sea and absence of intensive water redistribution between local sea areas (Fig. 1).

Vertical distribution of Cs-137 in depth of a drill core is characterized by a decrease of its activity with depth. However, appreciable variations of activity on different depths were found. That can be related to different rate of sediment movement in these regions. Comparison of the obtained data on the specific activity of Cs-137 in local

areas (Table 1) with previous results shows, that by now the horizontal movement of water mass caused dissipation of "patches" of high activity of radionuclides in the sub-surface layer of sea water, observed in 1986 and 1987 years. It, in turn, caused throughout decrease of the content of this radionuclide in water. Owing to notable enclosedness of the sea, the present concentration of Cs-137 in the Baltic Sea is appreciably higher than that of the adjacent North Sea, although radioactivity of Cs-137 in the North Sea was higher than the level of nuclear pollution of the Baltic Sea before the Chernobyl accident. In contrast to the distribution of Cs-137, concentration of Sr-90 did not significantly change and structure of its concentration fields is similar to that before 1986 year.

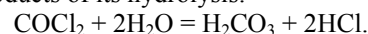
Table 1.

Years	1986	1987	1989	1990
<i>Baltic Sea regions:</i>				
Central part	134 ± 40	131 ± 40	115 ± 45	125 ± 49
South-eastern part	162 ± 48	144 ± 66	145 ± 57	130 ± 52
Water area a within Russia	186 ± 60	170 ± 50	126 ± 49	116 ± 45

Insignificant rate of self-purification of the sea area can be explained both by shallowness of the Baltic Sea and by some geochemical features of bottom sediments. In the Baltic Sea, which is the sea of a positive water balance, water supply into basin, located in humid zone, by sediments and river drainage is higher than the loss by vaporization. Development of halocline at some conditions accounting for vertical and horizontal gradients of salinity, can result in anoxia. In turn, it results in changing in redox conditions and appearance of hydrogen sulfide. As a result, decrease of sorption ability of sediments with respect to nuclear isotopes and equilibration of exchange of radionuclides between sediments and solid phase can occur.

Distribution of chemical parameters in the sub-surface layer of water is regular enough, with local variations, which firstly correspond to geographic location and hydrophysical conditions in the regions of probing. Significant variations of different parameters are not identified in sub-surface waters in the regions of storage of poison compounds in comparison to the "phone" areas.

Excess concentration of chloride ions (Table 2) were found in probes of bottom water in the regions of storage of poison compounds in the Gotland and the Borholm areas. It implies the presence of poison compounds (phosgene, in our case) in this region and, as a result, products of its hydrolysis:



The deeper horizons of the drill core are the most informative for bottom sediments (Table 3). According to x-ray fluorescence spectral analysis, the significant excess of arsenic, which is a constituent of lewisite, is identified for the Liepāja storage on the level 10-11. The excess content of elements, which are constituents of weapon bodies, is characteristic for the Bornholm storage.

Table also shows, that sub-surface layers of sediments do not show significant excess of technogenic pollution. Such excess does not also appear in bottom and mud waters (the results are obtained on the ship using the Reznikov's hydrochemical laboratory).

The obtained data show, that the revealed pollution of bottom sediments are local enough and are not identified in the upper layers of sediments and in bottom water, at least, in the studied regions. An analysis of the obtained results, accounting for geochemical data on the rate of sedimentation in the Baltic Sea, allows to assume, that chemical weapon, stored in the Liepāja and the Bornholm regions after the war by sinking of separate shells onto bottom, can not promote a loading on an ecosystem in the present time. It is attributed to the screen influence of covering surface of bottom sediments, as well as to sorption of different elements, firstly, hydrolyzed in sea water, and nuclear isotopes by muddy surface of bottom sediments. Moreover, the products of hydrolysis of poison compounds, which are simple inorganic compounds, are not toxic.

Another situation can be observed in places of storage of poison compounds in the Skagerrak and the Kattegat straits. In the case of possible depressurization of shells, the spontaneous input of poison compounds can take place. That can lead to significant pollution of environment. However, final conclusions about ecological situation in these regions can be done only after natural investigations.

Table 2.

№	№ St.	Station location	Horizon	pH	Cl, g/l	F, g/l
1	33	Gotland depression, Liepāja storage	Surface layers, Bottom water	8.2 7.12	5.39 8.29	3.48 3.27
2	34	Gotland depression. "phone" station	Surface layers. Bottom water	7.4 7.51	5.41 6.77	3.35 3.48
3	36	Borholm storage	Surface layers. Bottom water	7.91 7.33	6.10 11.26	3.5 4.12
4	37	Borholm storage	Surface layers. Bottom water	7.97 7.29	6.81 11.69	4.9 2.05
5	38	Borholm storage	Surface layers. Bottom water	7.41 7.24	6.56 6.63	3.08 3.15

Table 3.

Station location	Station number (depth, m)	Layer (cm)	Sr	Rb	Pb	As	Br	Zn	Cu	Ni	Co	Cr	V	Ba	Fe	Mn	Ti
Gotland depression, "phone" station	34	10-11	100	160	78	26	320	170	<10	48	26	100	42	0.069	3.4	0.030	<0.01
Gotland depression. Liepāja storage	33 (120)	10-11	83	220	86	100	230	260	<10	35	36	98	36	<0.01	4.5	0.056	0.35
Borholm storage	36 (96)	10-11	210	190	86	20	270	250	<10	67	33	94	95	0.07	4.7	0.31	<0.01
Borholm storage	37 (90)	10-11	130	98	64	<10	230	240	<10	36	<5	25	62	0.046	4.7	0.29	0.3
Borholm storage	38 (sand)	10-11	280	65	65	<10	22	53	<10	18	<5	29	63	0.057	0.95	0.01	0.16