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Hazardous Waste Fixation by Synthesis of Sodalite from Kaolinite

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Stabilization and fixation of hazardous wastes are indispensable for environmental pollution control.In this paper, fixation of hazardous waste such as radioactive iodine was experimentally examined by synthesis of sodalite from kaolinite. Synthesis of iodine sodalite was carried out using kaolinite, NaOH and NaI mixtures after mixing and heating at various temperatures and times. Synthesis of iodine sodalite was checked by the X-ray powder diffraction. Fixation rate of iodine in the sodalite was determined by alkali fusion and leaching tests. From the alkali fusion test, actual fixation rate of iodine was about 72mass% of theoretical fixation rate at reaction temperature, 375K and reaction time , 24h . From leaching test,1.9mass% of iodine at most was leached from synthesized iodine sodalite during 24 hours. Stabilization and fixation of iodine by synthesis of sodalite was successfully carried out.

Key words : Waste fixation , Iodine , Kaolinite , Sodalite , Low temperature synthesis

1.INTRODUCTION

At the final stage of waste disposal system, it needs certain fixation technology of hazardous radioactive and chemical materials. In this study , fixation methods of ^{129}I which is thought as the most hazardous radioactive nuclide due to long half-life($1.57x10^7$[y]) were examined. Present main fixation technologies are summarized in Table 1[1,2]. Among various fixation technologies, sodalite synthesis has only possibility of ^{129}I retrieval from sodalite waste form whereas remaining technologies such as cement solidification and vitrification cannot retrieve ^{129}I from waste form due to homogeneous distribution of ^{129}I in waste form. Therefore, we focused sodalite synthesis method of which principle is immobilization of ^{129}I in a crystalline structure. As shown in Fig.1 iodine sodalite has formula $Na_8Al_6Si_6O_{24}I_2$ of which structure unit consists of a cage formed of AlO_4 and SiO_4 tetrahedra linked together by their oxygen atoms. In the center of the cage an I^- is surrounded by

Table1 Various Fixation Technologies of ^{129}I.

Fixation Method	Raw Material	Principle
Vitrification	Glass	Low leaching pf waste form
Matrix of Apatite	Apatite	Low solubility matrix of apatite
Cement Solidfication	Alumina cement	High distribution ratio of hazardous material
Sodalite Synthesis	$NaAlO_2$ SiO_2	Immoblization of hazardous material in a crystalline structure

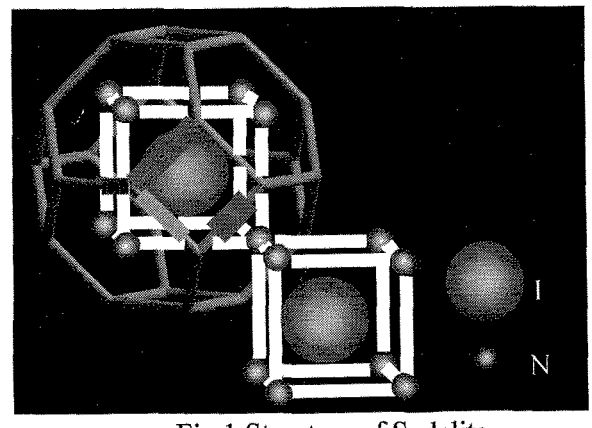

Fig.1 Structure of Sodalite.

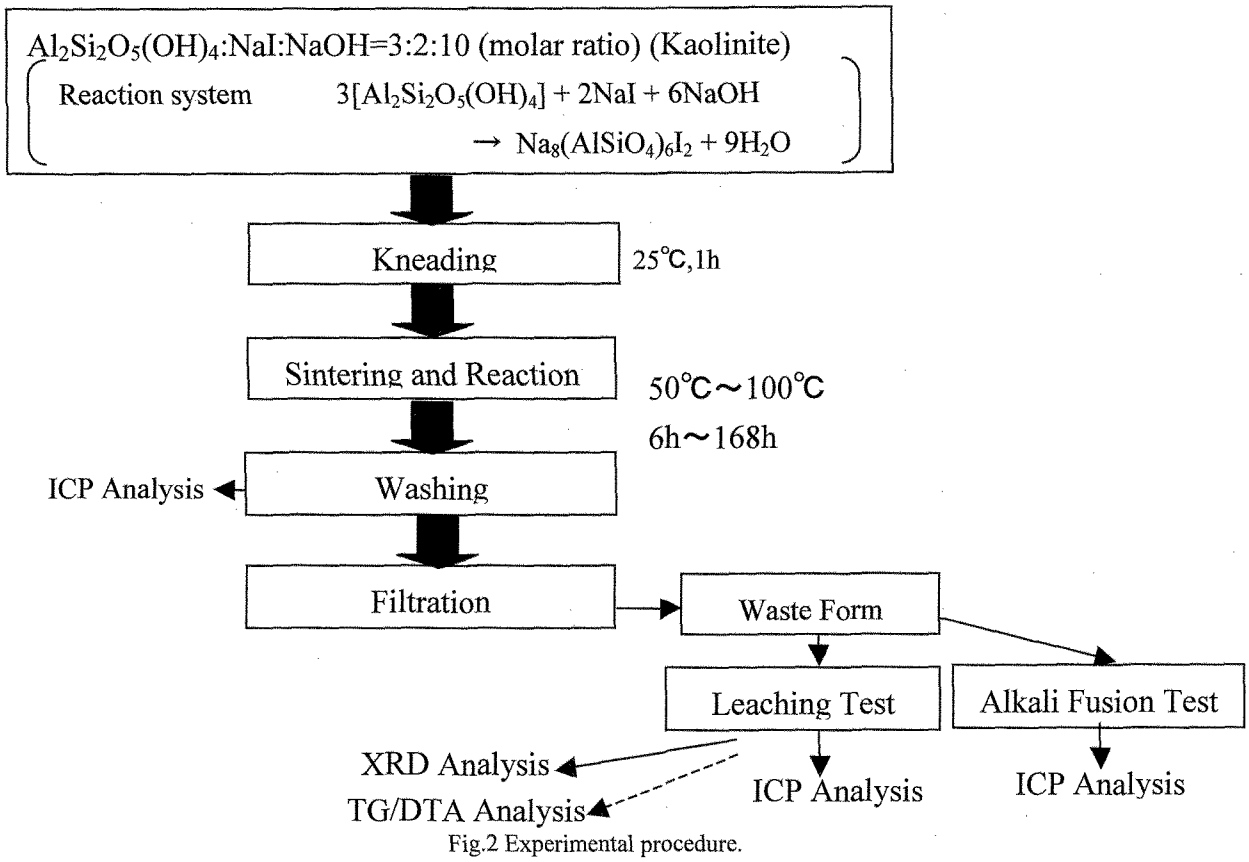

Fig.2 Experimental procedure.

four Na^+ ions[3].

Thus we employed sodalite as a fixation material of ^{129}I and Iodine sodalite was synthesized from kaolinite ($Al_2Si_2O_5(OH)_4$), NaOH and NaI at various reaction temperatures and reaction times[4] . We tried to synthesize sodalite at low temperature less than 100℃ and to immobilize iodine as a dominant radioactive waste in sodalite cystal.

Assessment of iodine fixation performance was carried out using leaching test from liquid phase and alkali fusion test from solid phase.

2.Experimental Procedure

2.1 Synthesis of iodine sodalite

Iodine sodalite was synthesized by mixing kaolinite ($Al_2Si_2O_5(OH)_4$) (Nisseikyoueki,Japan) and reagent grade NaI (Kanto Chemical Co.Inc.,Japan) in 10 M NaOH solution(solid-liquid ratio of 200kg/m^3),to give $Al_2Si_2O_5(OH)_4$: NaI molar ratio of 3:2.

$$3Al_2Si_2O_5(OH)_4 + 2NaI + 6NaOH \rightarrow Na_8(AlSiO_4)_6I_2 + 9H_2O \quad (1)$$

The slurry was dried for 6h to 168h at 30℃ to 100℃. Procedure of synthesis was shown in Fig.2 and reaction experimental condition was listed in Table 2.

Table 2 Experimental conditions.

Run	Reaction temperature[℃]	Reaction time[h]
1	100	6
2	100	12
3	100	24
4	50	24
5	50	72
6	50	168
7	30	168

2.2 X-ray diffraction

The RIGAKU-RINT2500VHF was used to obtain XRD patterns of solid products which were collected with CuK α radiation at 40kV/30mA. The diffraction

angle scans ranged from 10 to 60° (2 θ) with a speed of 5° (2 θ)per 1min.

2.3 Chemical analysis

The amount of iodine in the solids was determined using alkali fusion test and TG/DTA(ULVAC TGD9600). Concentration of iodine solution was determined using ICP-AES(Seiko Instruments Inc. SPS7700).

2.4 Leaching test

Batch experiments were performed in 100mL flasks containing 0.5g solid sample and 50mL distilled-deionized water,pH5 and pH9 solutions. The pH adjustments were made with HCl and NaOH. Each flask was shaken for 6 to 24h. After shaking , filtrate from each batch experiment was analyzed for iodine concentration by ICP-AES.

2.5 Alkali fusion test

A crucible made with Ni containing 0.5g solid sample and 4.0g(NaOH+KOH) was heated by a gas burner. After melting, iodine concentration in mother liquor was analyzed by ICP-AES. Fixation rate of sodalite was defined as follows.

$$\text{I fixation rate[mass\%]} = \frac{I\ concentratin[g/L] \times liquid[L])}{0.5g} \times 100[\%]$$

3.Results and discussion

3.1 XRD characterization

In Fig.3 , almost peak positions , especially at 2 θ =24° , of XRD patterns of solid at 100℃ , 24h(Run3) and solid at 50℃, 168h(Run6) matched well to values of natural sodalite . XRD pattern of Run7(30℃,168h) almost matched to that of kaolinite.

Lattice constants and full width at half maximum values(FWHM) for various samples are listed in Table 3. Run3 and Run 6 show lattice constants 0.90037 and 0.90096nm,respectively which are almost equal to iodine sodalite lattice constant,0.902nm.

FWHMs of Run3 and Run6 are so small compared to FWHM of Run7 that crystallinities of Run3 and Run6 are enough high.

Thus,it is expected that iodine sodalite is well synthesized at very low temperature such as 50℃.

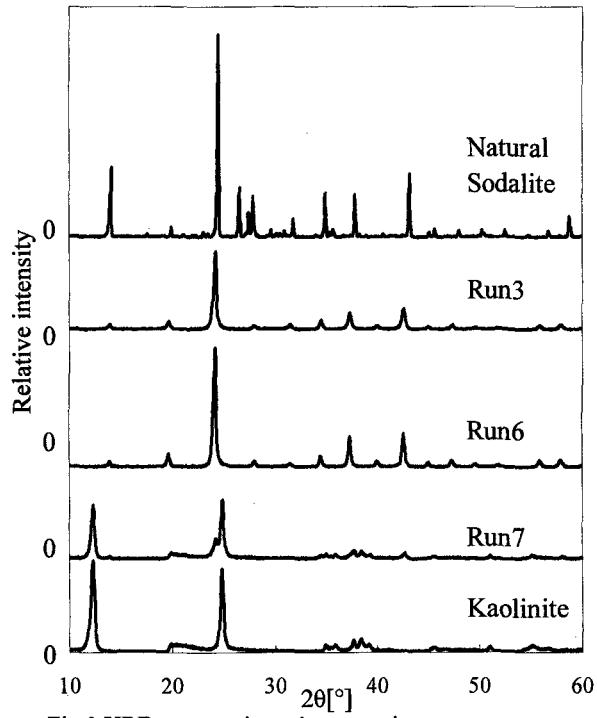

Fig.3 XRD patterns in various reaction temperatures.

Table 3 Lattice constants and FWHMs of various samples.

Sample	Lattice constant [nm]	Full width at half maximum at 2 θ =24°
Natural sodalite	0.88893	0.000
Run3(100℃,24h)	0.90037	0.183
Run6(50℃,168h)	0.90096	0.148
Run7(30℃168h)	0.89905	0.284

3.2 Leaching test results

Result of leaching test was shown in Fig.4. Iodine leaching amounts at time zero mean iodine amounts at washing of samples in Fig.2, in other words, unreacted iodine amounts adhered to the sample surface. Run2 shows leaching amounts of 6.43mg during about 5 hours

but zero leaching amounts hereafter. Run3 and Run6 showed that aqueous concentration of iodine was not changed during 24hours. This means that leaching amount of iodine from sodalite is almost zero. Almost same results were obtained at pH5 and pH9 solutions.

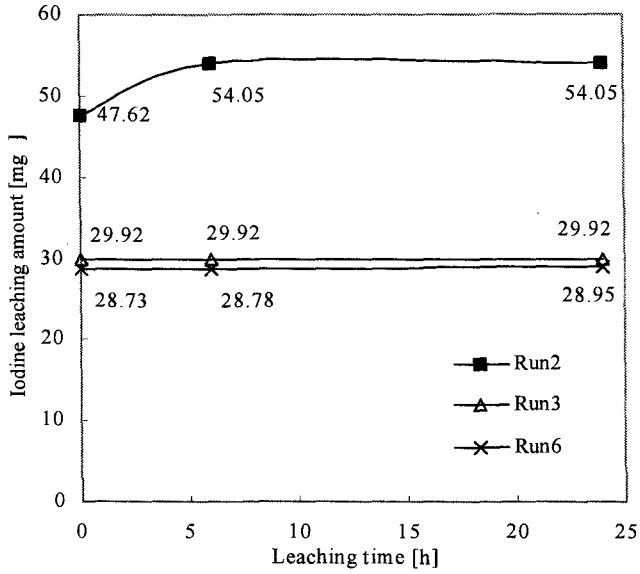

Fig.4 Relationship between iodine leaching amount and time.

3.3 Alkali fusion test results

From alkali fusion test , fixation rates of iodine in the solid products were obtained as shown in Fig.5.

Fig.5 shows dynamics of iodine sodalite synthesis. Fixation rate is improved more rapidly at 100℃ than at 50℃.

Best fixation rate in our experiments, 15.9mass%, means 72% of sodalite cages is approximately used for iodine fixation, whereas Nakazawa et al.[4] reported that about 11mass% was best fixation rate in their experiments.

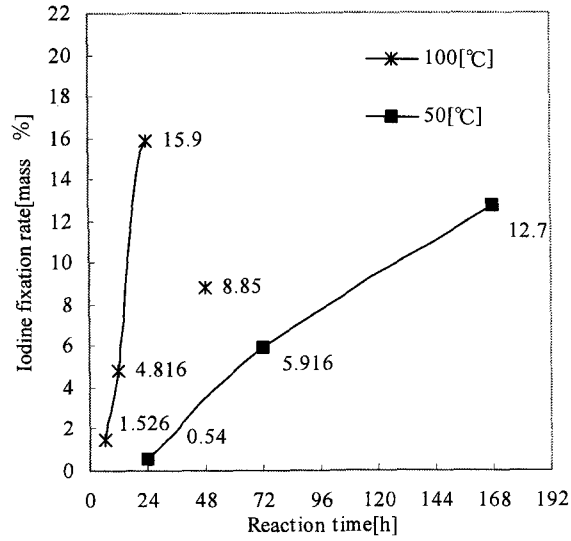

Fig.5 Alkali fusion test results.

4.Conclusions

From the synthesis experiment of iodine sodalite from kaolinite, following conclusions were obtained.

1.Sodalite was synthesized at very low temperature such as 50℃.

2.Alkali fusion test showed that best fixation rate was 72% of ideal value.

3.Leaching test showed that negligible amount of iodine was detected during 24h.

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