

## Alternative Sealing Materials for Radioactive Waste

### Longterm Storage or Disposal

Naohito Uetake, Tetsuo Fukasawa, Fumio Kawamura and Hideo Yusa  
Energy Research Laboratory, Hitachi Ltd.  
Hitachi, Ibaraki, 316 Japan

### ABSTRACT

The properties of  $\text{Ca}_3\text{SiO}_5$ -sodium silicate solution system solids were investigated for potential use in sealing radioactive waste. Preliminary experimental results showed that after autoclaving the solids had a high strength comparable to concrete while their ability to immobilize radioactive nuclides was better than concrete. Additionally, these solids were expected to offer superior chemical stability during the long periods required for safe radioactive waste storage and disposal. Based on these results, the  $\text{Ca}_3\text{SiO}_5$ -sodium silicate solution system can be considered as a good alternative sealing materials.

### INTRODUCTION

Requirements are strict for prevention of radioactive nuclide dispersion from waste longterm storage or disposal facilities. Therefore, radioactive wastes have usually been transformed into more stable forms such as glasses. To prevent radioactive nuclide dispersion from such wastes, several sealing methods have been investigated for one of engineering barriers which exist between waste and geologic media. They include overpack, grout and backfill. Suitable materials for sealing radioactive waste are commonly required to have the following characteristics:

- sufficient mechanical properties to endure stresses from geophysical changes occurring over long time periods;
- low porosity to prevent penetration of ground water and diffusion of radioactive nuclides;
- longterm chemical stability;
- large adsorption capability for easily leached nuclides;
- economically and technically convenient process to construct the sealing barrier.

As one such material, clay minerals have been proposed in several countries.<sup>1,2</sup> Concrete has also been proposed<sup>3</sup> as a possible encapsulation or overpack material, as it is superior in terms of points 1 and 5, although poor regarding points 3 and 4. Thus, we investigated ways to improve the properties of concrete. Concrete includes large amounts of  $\text{Ca}(\text{OH})_2$ <sup>4</sup> and its inducted harmful salts such as ettringite.<sup>5</sup> These compounds result in chemical instability. On the other hand, sodium silicate solution is set by several reagents and used for grout. Although these sodium silicate containing products have the ability to prevent water penetration, much attention has not paid for its mechanical properties. However, we tried to enhance their mechanical properties by choosing hardners.<sup>6</sup>  $\text{CaO-SiO}_2$  compound (e.g.  $\text{Ca}_3\text{SiO}_5$ : one of the main components in Portland cement) were found to have high chemical stability as well as good mechanical properties.

Therefore, we suggest that  $\text{Ca}_3\text{SiO}_5$ -sodium silicate solution systems as alternative sealing materials for radioactive waste longterm storage or

disposal. In the following sections, our preliminary results are described.

### EXPERIMENTAL

Chemical composition of the sodium silicate solution used was 13.4 wt%  $\text{Na}_2\text{O}$ , 26.2 wt%  $\text{SiO}_2$ , and 60.4 wt%  $\text{H}_2\text{O}$ . The  $\text{Ca}_3\text{SiO}_5$  used, was synthesized in the laboratory. A sample was ground to powder and analyzed by x-ray diffraction.

In order to form setting solids, sodium silicate solution and  $\text{Ca}_3\text{SiO}_5$  powders were mixed at room temperature, and poured into several cylindrical containers made of fluorocarbon polymer. After placing in an autoclave, the containers were heated at a certain temperature between 80 and 200°C under saturated water vapor conditions. As this treatment accelerated the setting reaction which occurred gradually at room temperature and required several months for completion, experiments could be carried out on a reasonable time scale. However, high temperature setting solids has a smaller volume change than room temperature ones. Therefore, it should depend on the required conditions in the barriers as to whether the treatment is practical or not.

Part of the set solids was cut into cylindrical blocks (diameter: 20mm; height: 40mm) and used for uniaxial compressive strength measurements, the  $^{134}\text{Cs}$  leaching tests and weathering examinations. A second part was smashed for measurements of its pore size distribution by mercury porosimeter and SEM fracture surface observations, and for measurements of the distribution coefficient of  $^{134}\text{Cs}$ . The rest was ground in an agate mortar for determinations of the x-ray diffraction pattern.

### RESULTS AND DISCUSSION

#### Mechanical Strength

The uniaxial compressive strength of the formed solids increased as heating temperature rose, but saturated at about 130-150°C. Therefore, it was considered that heating at about 150°C was required to complete the setting reactions within 5 hours. The uniaxial compressive strength of the setting solids increased with larger additions of  $\text{Ca}_3\text{SiO}_5$ . The relationships between strength and  $\text{Ca}_3\text{SiO}_5$  addition ratios are shown in Fig. 1. When the  $\text{Ca}_3\text{SiO}_5$ /sodium silicate solution ratio was 0.5 the strength was about 20 MPa. When that ratio was 0.8, the strength

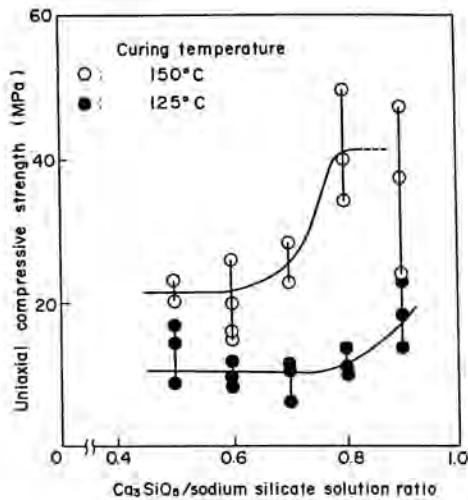


Fig. 1. The relationships between strength and  $\text{Ca}_3\text{SiO}_5$  addition ratio.

was higher and about 40 MPa. As more  $\text{Ca}_3\text{SiO}_5$  addition harmed workability of  $\text{Ca}_3\text{SiO}_5$ -sodium silicate solution system slurry, it becomes difficult to construct good solids. As the set solids' strength was comparable to concrete's, these solids could be used as a substitute for concrete.

#### Porosity and Microstructure

Total porosity of the formed solids decreased as the setting reaction was completed. The results of pore size distribution measurements for solids cured at 125, 135 and 150°C are shown in Fig. 2. The large peak at about 10 μm in the solid cured at 125°C, became smaller and disappeared in the solid, cured at 150°C. As this peak could be assumed to originate from the reactant  $\text{Ca}_3\text{SiO}_5$  particle gaps, the observation corresponding to progression of the  $\text{Ca}_3\text{SiO}_5$  hydration. However, curing above 150°C had no remarkable effect on pore distribution.

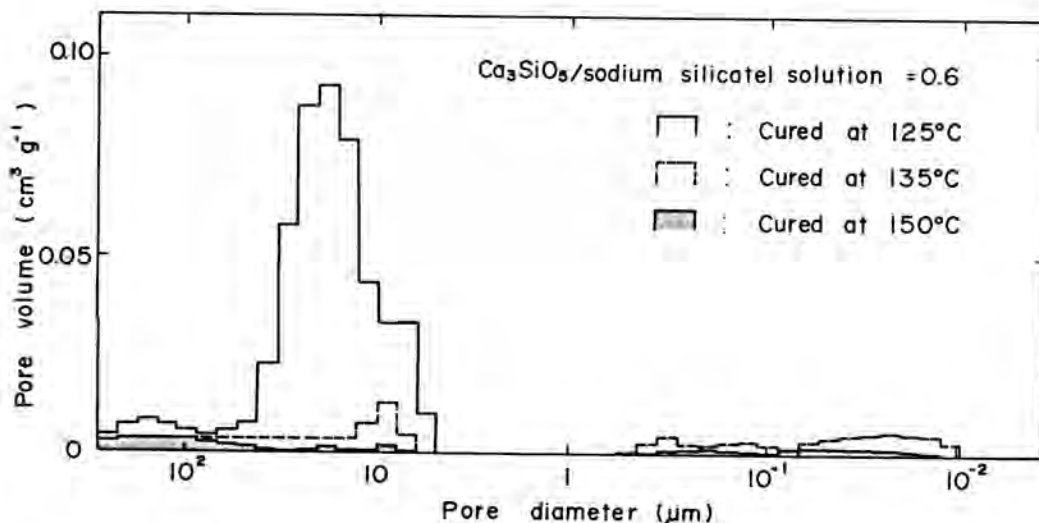


Fig. 2. The results of pore distribution measurement ( $\text{Ca}_3\text{SiO}_5$ /sodium silicate solution=0.6)

The SEM image of solids cured at 125, 135 and 150°C are shown in Fig. 3 and 4. The solids cured at 125°C showed many cracks. However, the solids cured at 135 and 150°C had only a few small pores and relatively flat fracture surfaces. These set solids were composed of fine particles (below 0.1 μm) and appeared more homogeneous than the microstructure of concrete. Measured porosity value of the set solids was smaller than values reported for concretes.<sup>7</sup> Therefore, the solid with a completed setting reaction was considered dense enough to resist penetration of groundwater.

#### Chemical Stability

In the setting reaction,  $\text{Ca}_3\text{SiO}_5$  became hydrated and then released  $\text{Ca(OH)}_2$ . Although this reaction was the same as in Portland cement, the released  $\text{Ca(OH)}_2$  reacted with silicate ions in the sodium silicate solution and incorporated them into  $\text{CaO-SiO}_2\text{-H}_2\text{O}$  system compounds. The x-ray diffraction pattern of the setting solids did not indicate any diffraction peaks from  $\text{Ca(OH)}_2$ , as shown in Fig. 5. The diffraction pattern of the solids corresponded most closely with tobermorite's. Tobermorite is a  $\text{CaO-SiO}_2\text{-H}_2\text{O}$  system compound and has high chemical and thermal stability. The  $\text{Ca(OH)}_2$  in Portland cement is known to be responsible for chemical instability. Carbon dioxide in air and sulfate salts in ground or sea water react with  $\text{Ca(OH)}_2$  and often destroy the concrete physical structure. The elimination of unstable  $\text{Ca(OH)}_2$  in the setting solids should enhance the chemical stability. However, in order to prove longterm chemical stability, weathering tests under various circumstances for long periods are required. Solids weathered in room temperature air did not indicate any visible changes over a 1.5 year period.

#### Adsorption Capability for Cs

After  $^{14}\text{C}$  and  $^3\text{H}$ , Cs is almost the only soluble long life nuclide contained in radioactive waste solids, and concrete cannot adsorb it. However, the distribution coefficient for Cs through the  $\text{Ca}_3\text{SiO}_5$ -sodium silicate solution solid showed a relatively high value as given in Table I. The  $^{134}\text{Cs}$  leaching test results in Fig. 6 show that the setting solids had a high ability to retain  $^{134}\text{Cs}$  in the solids due to the high distribution coefficient for Cs.

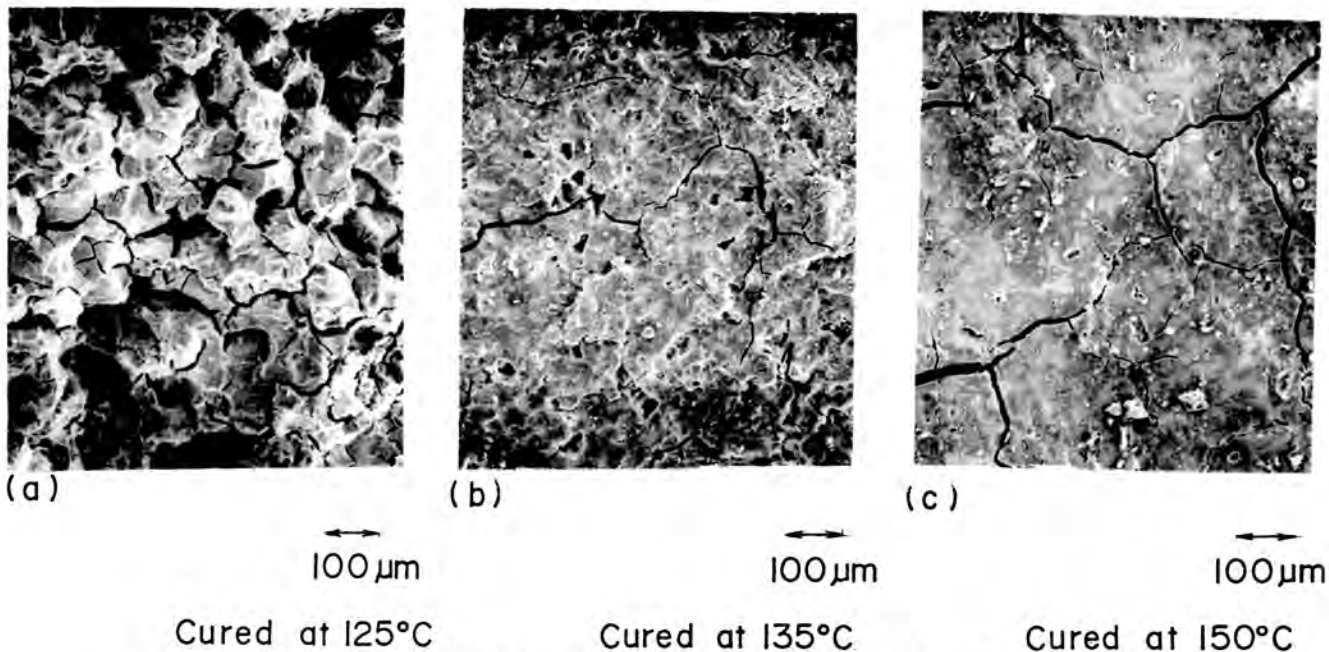


Fig. 3. The SEM images of fracture surfaces ( $\text{Ca}_3\text{SiO}_5/\text{sodium silicate solution}=0.6$ ).

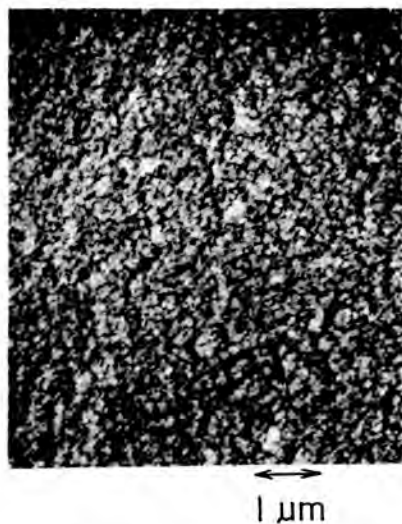


Fig. 4. The SEM Image of Fine Particles Constituted of the Cured Solid (cured at 150°C,  $\text{Ca}_3\text{SiO}_5/\text{sodium silicate solion}=0.6$ ).

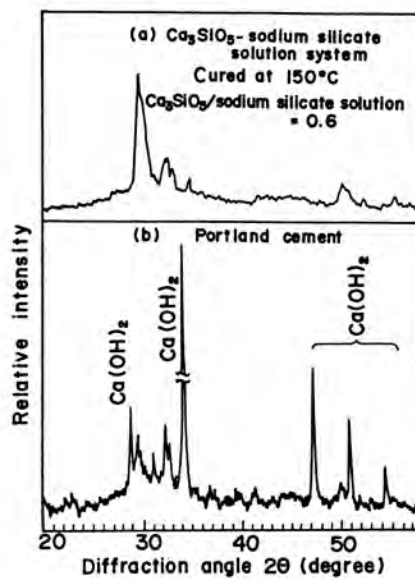


Fig. 5. X-ray Diffraction Patterns (CuK) of Setting Solids.

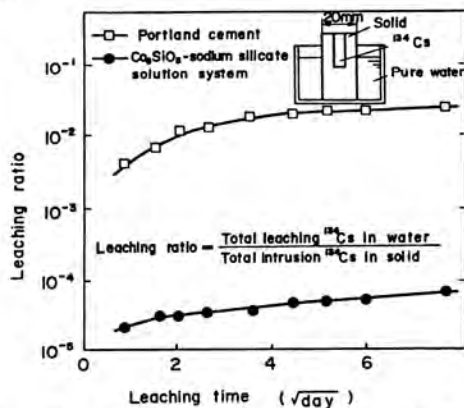


Fig. 6. The results of  $^{134}\text{Cs}$  leaching test.

TABLE I

Distribution Coefficients of  $\text{Ca}_3\text{SiO}_5$ -Sodium Silicate Solution System Solids and Other Materials

Sample	Distribution coefficient $K_d$ ( $\text{ml g}^{-1}$ )
$\text{Ca}_3\text{-SiO}_5$ -sodium silicate solution system solid	280
Portland cement	0
Blast-furnace slag cement (C)	1.3

## CONCLUSION

The above described preliminary results indicated that  $\text{Ca}_3\text{SiO}_5$ -sodium silicate solution system solids have comparable mechanical strength with concrete and, moreover, are expected to prevent radioactive nuclides dispersion and maintain good chemical stability. Therefore, the  $\text{Ca}_3\text{SiO}_5$ -sodium silicate solution system can be considered as a good alternative sealing material. However, final confirmation of its chemical stability requires further examination.

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