Characteristic evaluation of colloidal silica grout material developed for a high level radioactive waste geological repository

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高レベル放射性廃棄物の地層処分場へ適用するグラウト材料として，活性シリカコロイドを用いた溶液型材料が開発された。本材料の特長は，粒子サイズが 50 nm 以下と小さいこと，アルカリ性が低いことがあげられ，後者は長期間の地層処分場の安全性評価の不確実性を低減させる上で重要である。本材料は，活性シリカ溶液と硬化促進剤から構成されており，SiO_2 の濃度，粒子径，シリカの表面改質といった点について着目し各種試験を実施した。今回原位置への適用に向けて，粘性や寸法の安定，強度，水圧抵抗性といった基本的な物性と，シリカの溶出性に関する基礎的な室内試験を実施した。これらの試験の結果，本材料の地層処分場への適用性が高いことが示された。
Keywords: グラウチング，活性シリカコロイド，溶出，高レベル放射性廃棄物処分場，地層処分

A "Colloidal Silica Grout" (CSG) material has been developed as an alternative grouting material for the geological repository of high level radioactive waste. Two main advantages of the CSG are its smaller particle size distribution (< 50 nm) than those of the cementitious materials, and low pH so as to reduce unfavorable effects on the long-term performance assessment of geological disposal system. The CSG is a composed of a mixture of "colloidal silica solution" and KCl as hardening accelerator. The mixture being investigated for grouting materials was focused on SiO_2 concentration, grain size and degree of modified surface of silica. Preliminary laboratory experiments were carried out to characterize its fundamental properties from the viewpoint of viscosity, dimensions stability, compressive strength, pressure resistivity and leaching rate of silica. The experiments demonstrate that CSG is expected to become an alternative grouting material for a geological repository.
Keywords: grouting, colloidal silica, leaching, high level radioactive waste repository, geological disposal

1 Introduction

Grouting of the host rock is necessary to reduce amount of groundwater inflow into a geological repository of high level radioactive waste during the construction and operational phase because the geological environment in Japan is often characterized by many fractures and abundant groundwater. Basically, cementitious materials are conventionally used for grouting, however, the expected release of a high pH plume could alter the long-term performance of the bentonite buffer and the host rock. To mitigate these effects, JAEA has carried out the research and development of three alternative low pH grouting materials that decrease influence in the alteration: (i) Low-alkaline cementitious grout, (ii) Super-fine spherical silica grout and (iii) Colloidal silica grout [1]. The current work focuses on the Colloidal silica grout, and presents its unique characteristics obtained from a series of laboratory tests.

2 Requirement of inflow reduction by grouting

2.1 Evaluation model of grout treatment

Natural fractures in a rock mass take the form of complex shapes by variety of apertures and held clay in fractures, and penetrability of grout depends on geometric apertures of fractures. While hydraulic conductivity of a rock is needed to calculate amount of groundwater inflow, the hydraulic conductivity is estimated from hydraulic aperture which is averaged in consideration of above variable factors (Fig.1). The relationship between hydraulic apertures and geometric apertures is discussed by Alvarez et al based on measured data [2]. Based on the data, the relationship between the both apertures was estimated by the approximate expression (Fig.2).

The transmissivity of a fracture (T_f) with a hydraulic aperture "b" is expressed by

$$T_f = \rho g b^3 / 12\mu \tag{1}$$

Here, ρ is density of water and μ is viscosity of water.
The transmissivity of a host rock with plural fractures is expressed by

$$T = \sum T_f \tag{2}$$

Thus the hydraulic conductivity is expressed by

$$K = T/L$$

Here, K is hydraulic conductivity of the host rock and L is a length of an estimation section along a tunnel.
Therefore, the hydraulic conductivity of treatment area by grouting (K_i) is expressed by

$$K_i = T_i/L, \quad T_i = n\rho g b^3/12\mu \quad \text{on } b<b_G \tag{3}$$

Here, b_G is a minimum hydraulic aperture of fracture to be penetrable for grout and n is the number of b_G in the section.
The mount of inflow into the tunnel can be obtained by Eq.(4).

$$Q = \frac{2\pi \cdot K_i \cdot h}{\ln\left(\frac{R+t}{R}\right) + \frac{K_i}{K} \cdot \ln\left(\frac{2h}{R+t}\right) + \xi} \tag{4}[3]$$

Here, Q is the amount of inflow into the tunnel, R is a radius of the tunnel, t is a width of treatment area by grouting, h is overburden height, ξ is skin factor (2～7 in general) in consideration of pressure drop around the tunnel(Fig.3).

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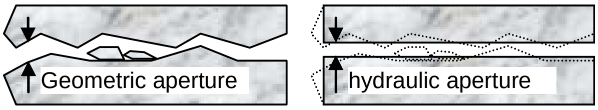
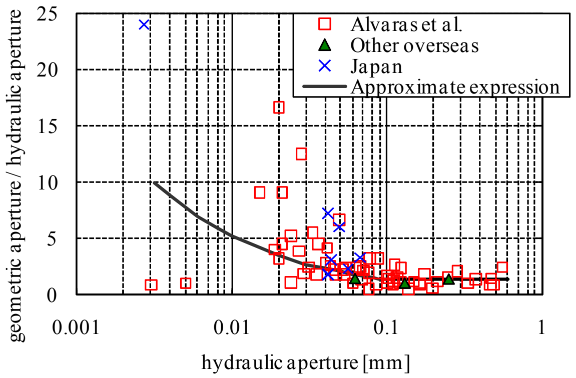


Fig.1 Geometric aperture and hydraulic aperture



[Approximate expression : $y = 0.357\log x - 0.580$ $(x < 0.1)$, $y = 1.356$ $(x \geq 0.1)$]

Fig.2 Result of literature survey on the relationship between geometric aperture and hydraulic aperture

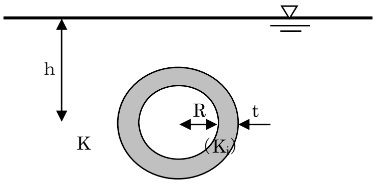


Fig.3 Calculation model of Eq.(4)

2.2 Requirement for grouting

On the parameters of tunnel depth (h), grout area (t) and skin factor (SF), the relationship between the minimum geometric aperture for the grout injection and the amount of inflow was calculated by Eq.(4) using the relationship in Fig.2 under the distribution of transmissivity (Fig.4) taken into account in the reference case in the report of R&D for a geological disposal of high level radioactive waste [4].(Fig.5) The density cases of fractures were set up as the number per meter of 0.1, 1, 10.

For reduction of the amount of inflow to a constant level, the more micro fractures have to be treated according to the increase in depth of a tunnel. The minimum geometrical apertures to be treated for reduction of inflow to 10 or 5*l*/min/100m are summarized in Table 1. According to this table, due to increase of fracture density, the more micro fractures are to be treated. And the minimum aperture to be treat is approximately 40 μm. The relationship between the minimum geometric aperture and the hydraulic conductivity of host rock is shown in Fig.6 to achieve the reduction of inflow to the amount of 5*l*/min/m. The relation suggests that the treatment is needed in the hydraulic conductivity of 10^{-9} m/s or more.

From results above-mentioned, the requirement for grout in a deeper geological repository has the treatment for micro fractures of 40 μm or under. Superfine cementitious grout is often applied to such treatment in general. However the grout is limited to use for such fractures of 50 μm or under [3]. Then CSG is needed to the treatment for the geological repository with greatly deep tunnels.

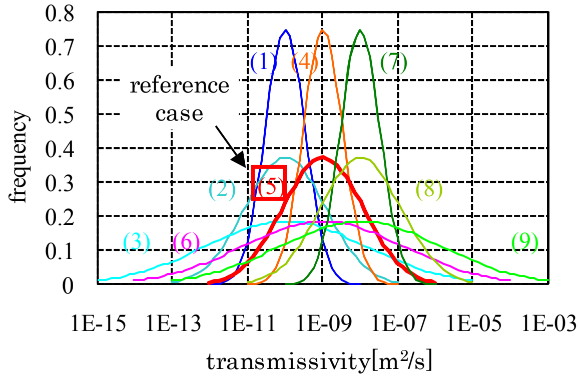


Fig.4 Transmissivity distribution used in this study

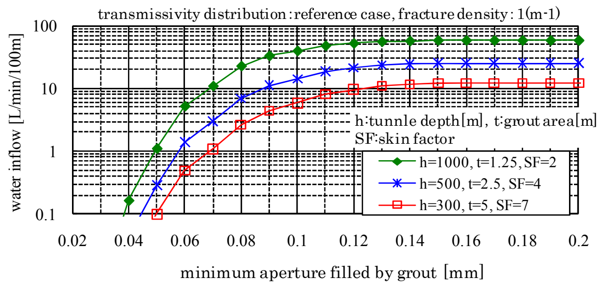


Fig.5 Relationship between water inflow and minimum aperture filled by grout (an instance)

Table 1 Allowable water inflow and minimum geometric aperture

		allowable water inflow [L/min/100m]	
		10	5
fracture density [m^{-1}]	10	40～90μm	40～70μm
	1	70～130μm	60～100μm
	0.1	90～240μm	80～230μm

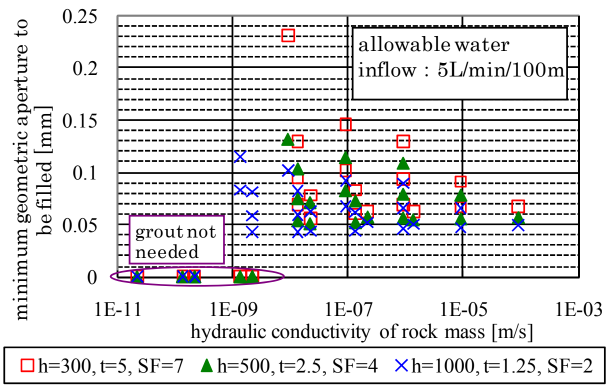


Fig.6 Relationship between hydraulic conductivity of rock mass and minimum geometric aperture

Table 2 Tested grout mixtures

Test Mix								Fundamental property tests			
Objective	No.	Hi silica (g)	Accelerator (g)	Water (g)	Silica content in grout (wt.%)	Grain Size (nm)	Remarks	Dimensions stability test	Compressive strength test	Short term leaching test	Pressure resistivity test
Effect of Silica concentration	1-1	905.60	16.33	191.83	16	10~20	-	○	○		
	1-2	970.40	14.68	192.65	24	10~20	-	○	○	○	○
	1-3	1040.00	13.68	193.15	32	15~20	-	○	○		
Effect of modification	2-1	905.60	12.14	193.93	16	10~20	Modified with Al	○	○	○	
	2-2	602.50	14.11	492.95	16	10~20	Modified with NH_3	○	○		
Effect of grain size	3-1	969.60	12.37	193.83	24	7~10	-	○	○	○	
	3-2	606.00	15.60	492.20	16	7~10	-	○	○		
Foreign product	4	1040.90	145.73		24	10~20	-	○	○	○	

3 Laboratory tests on the fundamental properties

3.1 Test cases

Laboratory tests were carried out to evaluate fundamental properties in several cases focused on SiO_2 concentration, modified surface of silica and grain size (Table 2).

3.2 Dimensions stability test

In this test, shape of test pieces of hardened CSG was measured in height and diameter cured at the 20°C and relative humidity of 98, 95, 80%. The shape of test pieces was modeled to a cylinder of ϕ50mm and 100mm height at first. The test pieces were cured in a constant temperature and humidity box for 100 days. The change rate of specimen height at the relative humidity of 95% is shown in Fig.7. The more the test piece had low concentration of silica, the more the dimensions shrank in the passage. Thus higher concentration of silica is necessary for CSG from viewpoint of dimensions stability relatively. The No.1-3, 4, 3-1 and 1-2 were considered to be better for the stability.

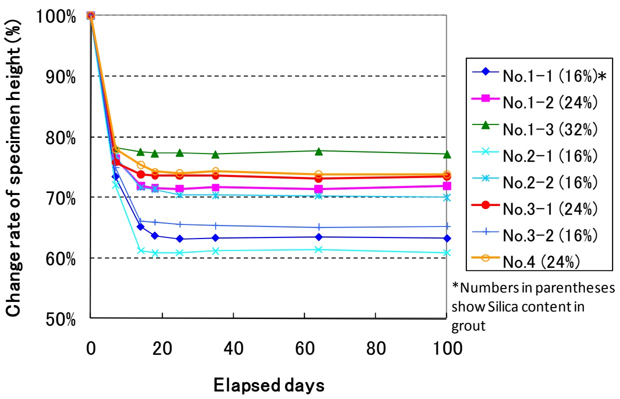


Fig.7 Change rate of specimen height (under the relative humidity of 95%)

3.3 Compressive strength test

The compressive strength tests, based on JISA1216, were carried out for the test pieces of ϕ50mm and 100mm of height cured at the age of 1, 7 and 28 days. The results compared in Fig.8 indicated that the silica concentration was an important factor to the strength, but the grain size was also another factor in combination with silica concentration. The No.3-1, 4 and 1-2 were considered to be better for the stability.

From these test results, it was found that the stability and strength was related to silica concentration and grain size. Then several mix cases which was considered to be better and modified surface case was selected for short term leaching test.

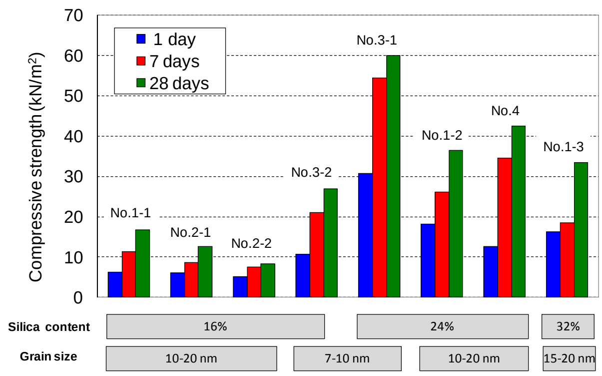


Fig.8 Uni-axial compressive strength

3.4 Short term leaching test

The test was conducted to evaluate the durability of CSG gel in water. The test method is described later in detail (standard test in 4.1). In the tests, the leaching of silica was measured monthly after gelation. As a result, the No.4 showed the highest leaching ratio of silica (Fig.9), however the results compared in Fig.8 indicates that the strength doesn't depend on silica concentration, grain size. The No.1-2 is considered to be better for durability.

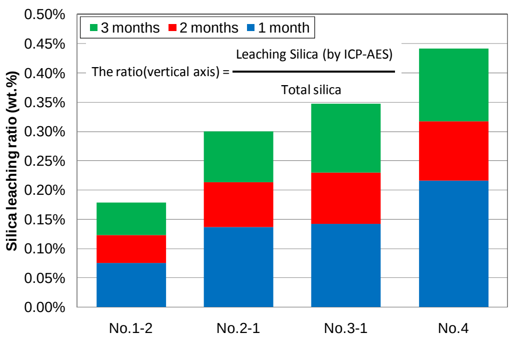
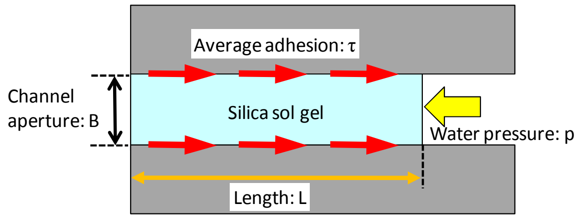


Fig.9 Silica leaching ratio

3.5 Pressure resistivity test

To evaluate resistivity against high pressure based on the evaluation model in Fig.10, the pressure resistivity tests were carried out by using parallel plates model in which the grout of No.1-2 was filled from 0.05 m to 0.2 m. The pressure at which the grout had leaved out of the plates was higher as the aperture was smaller and the span of the filled plates was longer (Table 3). Therefore, from the nano grain size and the above resistivity, it is considered that CSG has high penetration to micro fractures at high hydrostatic pressure.



➤Average adhesion

$$\tau = \frac{B \times p}{2L}$$

Fig.10 Assumed resistant model

Table 3 Resistant strength against water pressure

Test case	Channel aperture	L(m)	P (MPa)	τ (kPa)
CASE-1	100μm	0.05	1.56	1.56
CASE-2		0.10	＞3.0	＞1.5
CASE-3		0.20		＞0.75
CASE-4	200μm	0.05	0.50	1.00
CASE-5		0.10	0.94	0.94
CASE-6		0.20	1.05	0.53

4 Long term leaching test

4.1 Test method

Both standard test and acceleration test were carried out as below. Three types of CSG; No.1-2, 2-1 and 3-1(Table 2) were selected from results of fundamental tests.

Standard tests: The mixtures were cured by 100 mL in capped 200 mL flasks with 100 mL distilled water at 20°C respectively. The whole curing water was picked up and analyzed monthly.

Acceleration tests: The specific surface of gel was more expanded to accelerate the leaching of silica, and the curing water to the volume of gel was added to delay the saturation of silica in the water. In detail, 40 mL of CSG was mixed in a Petri dish (φ70mm) and the grout was cured in 3,000 mL distilled water for 1 month respectively. After the curing, the half of the water (1500 mL) was sampled and analyzed, and 1,500 mL distilled water was added to the remainder respectively. To evaluate long-term stability for 1 year and more, the test pieces were cured at the 55°C and relative humidity of 100% as heating accelerative curing based on the acceleration ratio referred to the past study on the same sort of grout [5]. Additionally, the grout of No.1-2 was cured for the term converted to 3 and 10 years (Table 4).

Analyses of the curing water: ICP-AES(Inductively Coupled Plasma-Atomic Emission Spectrometry) and IC(Ion Chromatography) were conducted for total silica and hardening accelerator.

Curing water / grout=1(volume)　　Curing water / grout=75(volume)

Fig.11 Curing Condition（Left；standard test，Right；accelerating test）

Table 4 Curing condition for accelerating test

Curing condition	Standard (20℃)	Accelerating curing (55℃, 100%RH)		
Curing time	1 day	12 days	36 days	120days
Converted curing time	0 year	1 year	3 years*	10 years*
No.1-2	●	●	●	●
No.2-1	●	●	—	—
No.3-1	●	●	—	—

*30 is assumed as acceleration rate of time passage according to reference [5].

4.2 Results and discussion

Results of long-term leaching tests are summarized below.

Standard tests: The leaching of total silica is shown as monthly leaching ratio and accumulated leaching ratio in Fig.12. The profiles of monthly leaching ratio show a peak at 5 or 6 months passage. The relationship between pH and total silica concentration in the curing water is shown in Fig.13. Additionally, the relationship between pH and saturated concentration of amorphous silica is shown in Fig.13 accordingly to the data of a past study [6]. The plots in Fig.13 indicate that total silica concentration in the curing water is nearly equivalent to the saturated concentration of amorphous silica. Thus, this result suggested that the leaching of total silica depends on leaching of amorphous silica. Also, the plots show that the curing water had low pH less than 11 that was target value. The accumulated leaching ratios of hardening accelerator in Fig.14 indicate that almost had leached in 15 months.

Acceleration tests: Accumulated leaching ratios of the acceleration tests are shown in Table 5. In this table, a passage term is equal to the sum of accelerated correspond term and measuring term. The monthly silica leaching ratios in Fig.15 indicate that No.1-2 has higher durability against leaching and No.2-1 and No.3-1 have lower durability in early period especially. As the result of the standard and accelerating tests, No.1-2 has the most applicability as the long-term durable grout material for a deep geological repository.

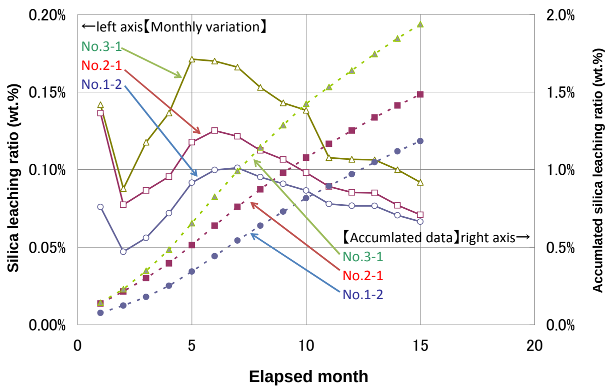


Fig.12 Silica leaching ratio (standard test)

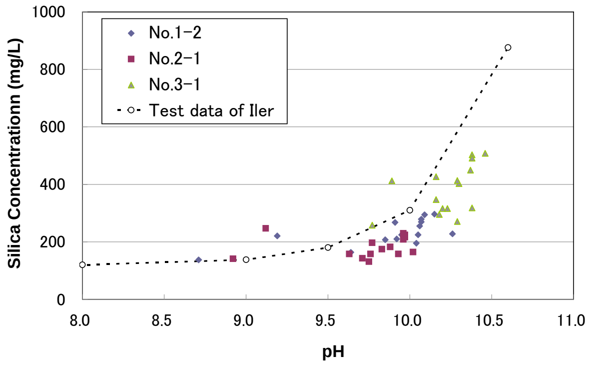


Fig.13 Silica concentration and pH of curing water

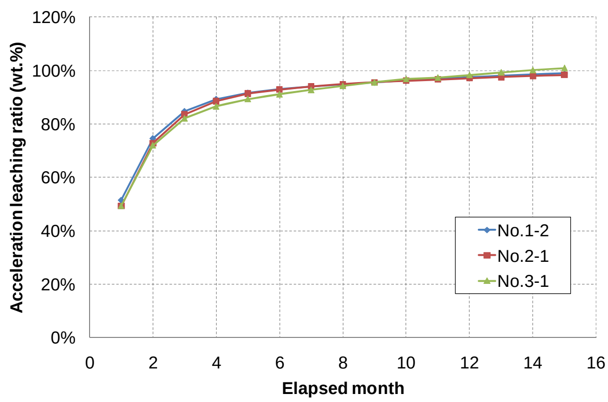
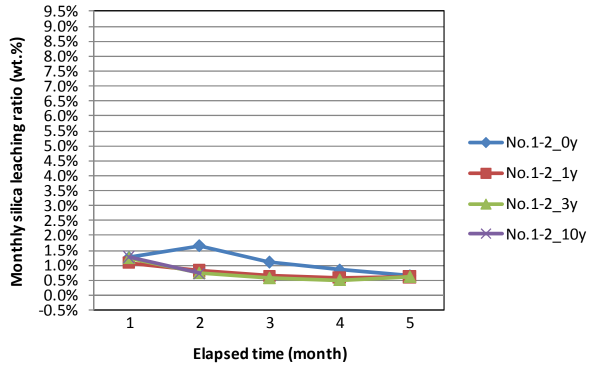
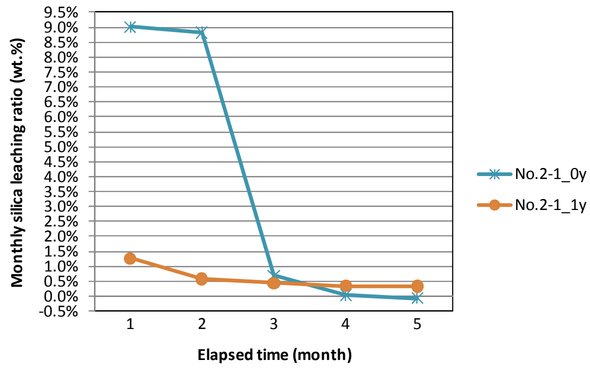


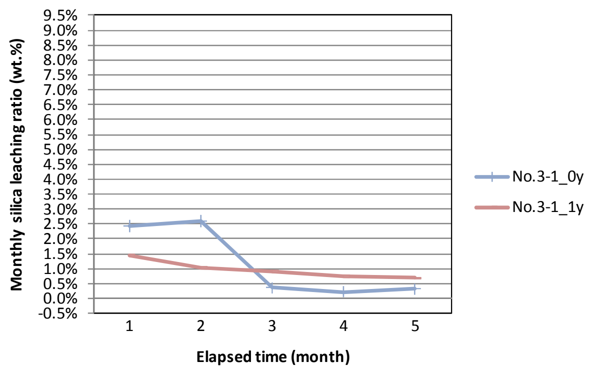
Fig.14 Leaching ratio of accelerator (standard test)



(a) No.1-2



(b) No.2-1



(c) No.3-1

Fig.15 Monthly silica leaching ratio

Table 5 Accumulated silica leaching ratio (accelerating test)

Converted curing months	0	1	2	3	4	5		12	13	14	15	16	17		36	37	38	39	40	41		120	121	122
Mix1−2_0y	0%	1.26%	2.91%	4.02%	4.87%	5.53%																		
Mix1−2_1y	Accelerating curing corresponding to 1 year							0%	1.08%	1.91%	2.55%	3.14%	3.76%											
Mix1−2_3y	Accelerating curing corresponding to 3 years														0%	1.25%	1.99%	2.56%	3.06%	3.67%				
Mix1−2_10y	Accelerating curing corresponding to 10 years																					0%	1.28%	2.01%
Mix2−1_0y	0%	9.02%	17.84%	18.52%	18.56%	18.49%																		
Mix2−1_1y	Accelerating curing corresponding to 1 year							0%	1.26%	1.84%	2.28%	2.61%	2.95%											
Mix3−1_0y	0%	2.43%	5.02%	5.37%	5.59%	5.90%																		
Mix3−1_1y	Accelerating curing corresponding to 1 year							0%	1.46%	2.47%	3.36%	4.11%	4.79%											

5 Conclusions

CSG has very small grain size of nano-order to be good penetrable into micro fractures. The grout is considered to be a alternative material for cementitious materials. The series of laboratory tests to evaluate the fundamental properties and leaching of colloidal silica grout (CSG) were conducted. From the results, the better mix(No.1-2) was selected for in-situ grouting. We are planning to confirm its applicability to the geological disposal of high level radioactive waste.

Acknowledgments

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