Decontamination Method of Ground Based on SilicaTech® Coating Technique

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The TEPCO (Tokyo Electric Power Corporation Holding Inc.) Fukushima-Daiichi Nuclear Plant Accident in March 2011 has contaminated wide areas of east Japan with the radioactive substance. New idea has been created to use a SilicaTech® coating technique which was based on the Sol-Gel method to decontaminate soil of the ground. The liquid of the SilicaTech® coating technique with high permeability can penetrates into any depth and solidify the soil layer. The solidified soil can be easily dug without missing the contaminated soil nor taking extra of clean soil. The decontamination test was successfully performed at the Watari Elementary School in Fukushima-city. The radioactive cesium depth on 16 May, 2011 was found to be 1.5 cm and in consistency with the geometrical averages of later data reported from the Ministry of Environment in 2016.

KEYWORDS: Decontamination, Radioactive Cesium, Glass, Sol-Gel Method, Fukushima, Siloxane Bond,

1. Introduction

In March 2011, environments of east Japan were contaminated due to the TEPCO (Tokyo Electric Power Corporation Holding Inc.) Daiichi NPP (Nuclear Power Plant) accident by radioactive isotopes. Iwamiya, originator of Mizuhiki-art[1] that was characterized by decorative Japanese code made from twisted paper, has developed a new method to decontaminate radioactive cesium fallen out to the ground by using her SilicaTech® coating technique[2] based on the sol-gel procedure. The experiments made at the Watari elementary School in Fukushima city clarified the high applicability.

2. Sol-Gel Procedure in Present SilicaTech® Coating Technique

The SilicaTech® coating technique is based on the sol-gel processing[2]. Sol-gel processing is beneficial in the formation of ceramic and glass films of various functions and applications. The sol-gel process consists[3] of a series of hydrolysis and condensation reactions of an alkoxide, which proceed according to the reaction scheme shown in Fig. 1. Here, alkoxy silanes are used as an example but all of the metal alkoxides react similarly. While hydrolysis is initiated by the addition of water to the silane solution in ordinal sol-gel method, any water is added to the mixture solution of
main alkoxylane, metal alkoxides as a catalysts, functional auxiliaries and solvent in the present SilicaTech® coating technique; hydrolysis is initiated by using water contained in the coated objective or in the environment in the present method. This method induces a slow sol-gel reaction and results in a perfect glass to be expected. Sol-gel reactions do not employ extreme reaction conditions. The reactions take place at room temperature and require only moderate temperatures to ‘cure’ the gel, removing the solvent and water/alcohol that the reaction generates. Through sol-gel processing, homogeneous, high-purity inorganic oxide glasses can be made at ambient temperatures conventional approaches. Various products, such as molded gels, spun fibers, thin films, molecular cages, and xerogels can be developed for utility in such areas as gas separations, elastomers, coatings, and laminates[3].

Mixture solution has low viscosity and high permeability in substance. After coating the objective material such as organic paper and tree or inorganic metal and mineral which should be coated with the solution, the solution penetrates through material through pin hole or narrow gap (if it exists) and vitrifies around-and-in the material through the Sol-Gel procedure together with the siloxane bond between them through dehydration reaction as shown in Fig. 2.

![Fig. 1. Sol-Gel Reaction Scheme](image)

\[
\text{Hydrolysis} \quad \equiv \text{Si-OR} + \text{H}_2\text{O} \rightarrow \equiv \text{Si-OH} + \text{ROH} \quad (1)
\]

\[
\text{Alkoxylane} \quad \text{Water} \quad \text{Silanol (Sol)} \quad \text{Alcohol}
\]

\[
\text{Water} \quad \equiv \text{Si-OH} + \text{HO-Si} \rightarrow \equiv \text{Si-O-Si} \equiv + \text{H}_2\text{O} \quad (2a)
\]

\[
\text{Codensation} \quad \text{Silanol} \quad \text{Silanol} \quad \text{Siloxane (Gel)} \quad \text{Water}
\]

\[
\text{Alcohol} \quad \equiv \text{Si-OH} + \text{RO-Si} \rightarrow \equiv \text{Si-O-Si} \equiv + \text{ROH} \quad (2b)
\]

\[
\text{Condensation} \quad \text{Silanol} \quad \text{Alkoxylane} \quad \text{Siloxane (Gel)} \quad \text{Alcohol}
\]

![Fig. 2. Siloxane bond between glass film and objective](image)

3. Decontamination Method and Experiment at School Ground

The basic concept of the decontamination is as follows: The SilicaTech® glass solution is selected by considering that it has high permeability into soil and to easily bond to the soil even at low temperatures. After spraying the liquid on the ground, it penetrates the soil layer through a very narrow gap as like silicone. The penetrated liquid can solidify the soil by bonding to the soil and becoming glass up to the
penetrated depth and incorporating radioactive material into the glass layer. The solidified layer can be easily removed.

A trial experiment to solidify and remove the non-active soil was made at Yokohama in April 2011. The experiments showed that the soil layer thickness to be solidified could be well controlled by amount of the sprayed solution. Actual decontamination experiments on the schoolyard of Fukushima municipal Watari Elementary School on 16, 17 May 2011, when it was two month later after the NPP accident. On the first day, alcoxilane liquid was sprayed by different amounts from 50 to 150 cc per m² in five places with each 1 m² area of the school ground in front of the main school yard. Next day, the solidified topsoil was lifted and peeled-off with a trowel. Fig. 3 shows the solidified topsoil which cold easily peeled-off without removing extra soil from the ground. The peeled-off soil thicknesses were 1.3-1.7 cm. Radiation doses on the ground before and after removing activated soils were measured 5 times in each section with a handy type photon detector with CsI(Tl) scintillators, “Hakarukun” shown in Fig. 4. The detector was located at the height of about 1 cm from the ground for a few minutes for which measured value became stable.

Table I shows results for radiation dose rates of each section of the ground before and after peeling off the topsoil as a function of amount of sprayed liquid. The thickness of the peeled-off soil layer increased linearly to amount of sprayed liquid from 50 to 250 cc/m². Reduction rates of dose rates after to before peeling off decreases as an increase of amount of the sprayed liquid. Fig. 5 shows that the decontamination rate is increasing with the liquid and approximately saturated to 150 cc/m² where the peeled thickness was about 1.5 cm. Accordingly, the penetration depth of radioactive

<table>
<thead>
<tr>
<th>Sprayed liquid (cc/cm²)</th>
<th>Dose Rate before Peeling (µSv/h)</th>
<th>Dose Rate after Peeling (µSv/h)</th>
<th>Dose Reduction Rate (%)</th>
<th>Decontam. Rate (%)</th>
<th>Peeled Soil Thickness (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>3.27</td>
<td>2.06</td>
<td>61</td>
<td>39</td>
<td>1.3</td>
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<tr>
<td>100</td>
<td>3.20</td>
<td>1.59</td>
<td>50</td>
<td>50</td>
<td>1.4</td>
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<td>150</td>
<td>3.31</td>
<td>1.10</td>
<td>33</td>
<td>67</td>
<td>1.5</td>
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<tr>
<td>200</td>
<td>3.38</td>
<td>1.06</td>
<td>31</td>
<td>69</td>
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<tr>
<td>250</td>
<td>4.08</td>
<td>1.31</td>
<td>32</td>
<td>68</td>
<td>1.9</td>
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</table>
cesium in mid May 2011 can be guessed to be 1.5 cm.

Further experiments to investigate the elution of cesium in water from the solidified soil were performed by dipping the peeled soil in the water. The results showed any material did not elute into water. The solidified material had some flexibility and was not brittle. It means that the waste processing of the peeled-off top soil will be also easily carried out.

After the NPP accident, a liquid glass consisting of sodium silicate was used[4] to stop flow out of radioactively contaminated water by injecting into the ground beneath the leaking storage pit. The sodium silicate was expected to be applicable to ground decontamination. However, it is of strong alkali and has a defect of low penetration into the soil. Additionally, solidified glass is so brittle that it may be broken. On the other hand, SilicaTech® glass solution is superior to penetration into the soil as like silicone and can solidify newly Cs-contaminated layer as shown in Fig. 6. Thus, radioactive cesium will be almost perfectly decontaminated by removing the solidified soil layer as long as its bottom is below the Cs contaminated soil layer (i.e., the ground surface) shown on the left hand side of the figure. Generally, radioactive cesium distribution as a function of depth makes a high peak of which integrated density become more than 90% and low broad peak. For practical application of decontamination, we had better aim to solidify the layer of high peak.

![Comparison of decontamination treatment using solution](image)

**Fig. 6.** Comparison of decontamination treatment using solution

4. Discussion

A survey on the depth distribution of radioactive cesium released into the environment following the accident at the Fukushima Daiichi Nuclear Power Plant has been conducted[5] in Fukushima, southern Miyagi, and northern Ibaraki prefectures since December 2011. The depth (90% depth) from the soil surface where 90% of radioactive cesium deposited in the soil is plotted as a function of elapsed day since the accident. The geometric average is 4.1 cm as of August in 2015, and below 5cm. The distribution of radioactive cesium depends on the properties of the soil: kinds of soil, elapsed date after the accident and ground status such as decontamination, deep cultivation, and cracking. Among the clay in the soil, clay minerals and zeolite,
including vermiculite, have the property of strongly adsorbing cesium. Another measurements of the depth were made for various places in Fukushima Prefecture by K. Saito et al.[6] Many figures of spatial distributions of radioactive cesium were given for different places and times. They reported that 99% depth to sandy soil was 2 cm for example of work at Yamakiya of Kawamata-machi on February 27th in 2012.

Fig. 7 shows the radioactive cesium distribution depths measured at various places as a function of elapsed time after the NPP accident. In the figure, present result and that of Saito et al. at Yamakiya of Kawamata-machi on February 27th in 2012 are plotted. It should be noted that our data is nearly in consistence with the data of Saito et al. and the geometrical averages of the others, which are dispersed because of different soils such as sandy one as like school ground, andic horizon, high organic and volcanic soils or status of ground such as farm land to be much influenced by cultivation. They must be influenced by rain and snow.

Fig. 7. Radioactive cesium distribution depth in soils after the NPP accident

5. Conclusion

The SilicaTech® glass could solidify the soil contaminated by activated cesium, and decontaminate ground without stripping excess soil nor spilling soil by adjusting spraying volume of the solution. It was also found that Cs penetration depth was about 1.5 cm mid May 2011. Thus, it is applicable to decontamination of the ground after the NPP accident. Since the raw mixture solution of the SlicaTech® glass will be able to solidify any hazardous and harmful substances, it will be also to applicable to the decommissioning at the Fukushima Daiichi NPP. The glass has been verified not to melt in the experiment at high temperature of 600 degree in Celsius.

Acknowledgment

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References


[6] Kimiaki Saito, Kazuhiro Aoki, Yuo Tanihata, "3 Confirmation of depth distribution of radioactive materials in soil"