Freeze Technology for Nuclear Applications – 13590

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ABSTRACT

Freezing of soil materials is a complicated process of a number of physical processes:

- freezing of pore water in a thermal gradient,
- cryogenic suction causing water migration and
- ice formation expanding pores inducing frost heave

Structural changes due to increase of effective stress during freezing also take place. The over consolidation gives a powerful dewatering/drying effect and the freeze process causes separation of contaminates. Artificial ground freezing (AGF is a well established technique first practiced in south Wales, as early as 1862. AGF is mostly used to stabilize tunnels and excavations.

During the last ten years underwater applications of freeze technologies based on the AGF have been explored in Sweden. The technology can, and has been, used in many different steps in a remediation action. Freeze Sampling where undisturbed samples are removed in both soft and hard sediment/sludge, Freeze Dredging; retrieval of sediment with good precision and minimal redistribution, and Freeze Drying; volume reduction of contaminated sludge/sediment.

The application of these technologies in a nuclear or radioactive environment provides several advantages. Sampling by freezing gives for example an advantage of an undisturbed sample taken at a specified depth, salvaging objects by freezing or removal of sludges is other applications of this, for the nuclear industry, novel technology.

INTRODUCTION

Artificial ground freezing (AGF) is a well established technique first practiced in Wales, 1862 [1]. AGF is mostly used to stabilize tunnels and excavations but an increasing interest in using AGF for environmental protection [2] is shown, as well as to use freeze/thaw cycles for remediation of contaminated soils [3]. AGF has been used for excavations up to 45 m in diameter and 900 m in depth [1]. Traditional dredging techniques range from modified mechanical excavation dredgers to hydraulic dredgers [4]. Freeze Dredging is a novel dredging technique developed by Luleå University of Technology in cooperation with industrial partners. The main idea with Freeze Dredging is to stabilize the contaminated sediments or sludges by artificial freezing and then lift it up while frozen.

Freezing, when applied as AGF, is induced by freeze pipes driven through the ground, and in the pipes a refrigerant liquid circulates, having a temperature well below the freezing point. When using Freeze Dredging the challenge is to freeze material under the water surface, and then the removal of it while frozen. Freeze pipes are arranged in a fashion that enables freezing, lifting and unloading of the frozen material. Pipes are arranged in a rectangular or triangular structure and the construction is called freeze-cells. At the moment two basic cells are used: the vertical arrangement having pipes of a length corresponding to the depth of the contaminated sediment and the flat cell being placed at the surface of the sediment with pipes arranged in a horizontal manner (Figure 1). Soft sediments that are impossible to excavate in its natural state can be stabilized by freezing and the stabilization facilitates excavation. For dredging of sediments to a maximum depth of 0.5 m flat cells are normally used and for deeper remedial work vertical arrangements of freeze pipes is used. In the latter case, freeze stabilization and corresponding excavation might also be appropriate.

Fig. 1. Left freeze cell with vertical freeze pipes, right flat freeze cell.

The brine circulating in the freeze cells are kept at a temperature of -15 to -25°C by the use of a mobile freeze plant.

The time needed for a complete freeze cycle depends on many factors. The most important are: temperature of the brine, thermal properties of the sediment, and the type of freeze-cell used. The time of a cycle can vary from a few hours to up to 5 days depending on the chosen design. For

THE FREEZING PROCESS

Freezing of soil materials is a complicated process of a number of physical processes: freezing of pore water in a thermal gradient, cryogenic suction causing water migration and ice formation and thus expanding pores and inducing frost heave. Structural changes due to the increase of effective stress during freezing also take place. The basic principle is that ice crystals grow by incorporating water molecules only. Because the structure of ice crystal is highly organized and symmetrical, it cannot accommodate any other atoms or molecules. Each ice crystal continues to grow as long as water molecules are available. All other impurities and solid particles are forced to the boundaries of the ice crystal where they become compressed or dehydrated. The efficiency of the process depends mainly on: the

1) mineralogical composition

2)size and shape of the particles

3)load,

4) hydraulic conductivity,

5)permeability,

6) porosity of the soil structure and

7) freezing conditions i.e. initial soil temperature, thermal properties, freezing temperatures, energy removal rate, [5, 6, 7].

Halde (1980) [8] reported that when freezing rate is slow enough, particles of nearly all materials are rejected by the moving ice–water interface. Thus the dewatering potential of the freeze-thawed material is greatly improved. On the contrary, when the freezing rate is high, particles in the solution are trapped into the developing ice layer resulting in little improvement of the capacity to dewater the sludge because the particles are not compressed or dehydrated. Corte (1962) [9] showed that fine particles migrate under a wide range of freezing rates and coarse particles migrate only at low freezing rates. This means that large particles are more likely to be trapped in the advancing ice front compared to the smaller particles.

DEWATERING

Water in saturated soil materials exists in different forms; the classification given by [10] will be used in this study. “Free” water is not associated with the aggregates and thus free to move; free water is easily removed with conventional mechanical dewatering systems. The water that is trapped inside an aggregate or is held by capillary forces is called “interstitial” water; a mechanical dewatering device can break the aggregate and free the interstitial water. “Surface” water is associated with the single particle by superficial forces. Mechanical systems, like belt filter press or dewatering centrifuges, can easily remove free water, interstitial water but can hardly remove superficial water. The fourth type of water can be released from the particles only with a thermo-chemical treatment and is called “bound” water (chemically bonded to the particles). In Figure 2 the four types of water are shown.

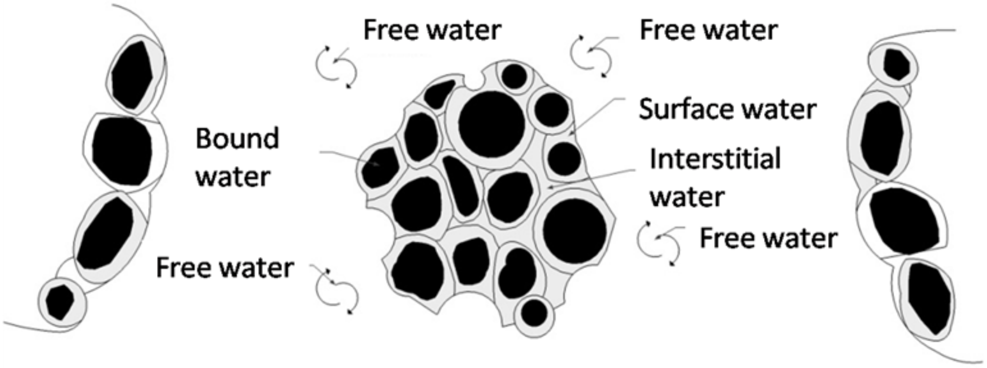

Fig. 2. A model for water distribution in a saturated soil material [10].

The effects of the freeze/thaw cycle are well documented in literature. Many authors have studied this treatment method and varied the type of sludge and external freezing configurations, freezing and thawing temperature, freezing rate and direction etc. in order to analyze and improve the dewatering potential. All the performed experiments have showed how freezing influences the sludge aggregates both physically and chemically i.e. size, shape and density of the aggregates and the bond water content. Freeze/thaw conditions are able to transform the bond water into free water and this water can then easily be removed by a mechanical method. The most dramatic effect of freeze-thaw conditioning occurs for inorganic sludges such as alum water treatment sludge [11]. The effect is irreversible, and the freeze-thawed alum sludge turns into a coffee ground like material that drains almost without resistance, producing a perfectly clear filtrate.

FREEZE SAMPLING

Freeze sampling is an excellent way of retrieving undisturbed sediment samples. The collection of undisturbed sediment cores is of great interest for many different research areas. Paleoclimatologists use data from undisturbed sediments for reconstruction of the history of lakes and their watersheds. Environmental researchers studies the distribution of contaminates and biologists determine the impact of grain size at lake bottoms for the fauna, figure 3.

Fig. 3. Environmental sampling from a pond of mine tailings, note the undisturbed layering of the sediments.

As the reliability of sampling with different types of core samplers can be questioned due to incomplete recovery resulting from a potential hydraulic shock wave or deficient entry of the sediment into the coring tube because of internal friction, freeze corers has been developed.

Using freeze sampling it is important to reflect over what impact the sampling technique can have on the material, and contaminates within it. To avoid alteration of the sludge fast freezing i.e. freezing of small amounts of material under low temperature is used. Vesilind and Martel, 1990 [10] suggest that a “fast freezing” rate, that does not exclude particles, can be defined as the rate were crystallization of the water molecules around the particle is faster than the net flow of water molecules into the structured layer. At this rate the particles becomes entrapped in the ice.

Chen et al., 2001[12] describes the “ultrafast freezing limit”, where the activated sludge flocks were found to be intact following freezing and thawing.

As freeze storage is a common way of preserving samples retrieved with other sampling techniques, freeze sampling is not expected to influence the results. Hjort 2004 [13], has studied how freeze storage affects sediments samples. He concludes that freeze-storage does not preserve the speciation pattern of major elements like S, Fe, Cu, Zn, phosphorus, and sulfur in anoxic lake sediment core sections. If this feature is important for the interpretation of data freeze sampling or freeze storage should be avoided.

CASE STUDIES NON NUCLEAR APPLICATIONS

Freeze dredging of very lose tar contaminated sediments, Luleå Sweden

The studied remediation project was carried out during autumn 2010 at the SSAB steel plant in Luleå, Sweden. Since 1975 SSAB operates a coking plant. It provides the unit with metallurgy coke and coke oven gas. During the coking process, early years large amounts of tar were transported out with the waste water. The tar was collected in a sedimentation step in a sewage ditch. Over the years many attempts had been made to excavate the contaminated sediment, they had failed since the sediment was too loose and volatile, using freeze stabilization prior to uptake this problem was solved.

The length of the ditch is approximately 230 m and the width approximately 9 m. The water depth varies between 0.5 to 1 m, see Figure 4. Preliminary investigations showed that a layer of 0.8 to 1 m of contaminated and very loose material had settled at the bottom of the ditch. The total amount of pollutants in the sediment is estimated to be approximately 28 tons of "hydrocarbon" of which approximately 8 tones is PAHs. The moisture content of the sediment was 50% as medium of 12 samples and the organic content in the sediment, as measured by loss of ignition, was 48% and 82% of DM in the two samples studied. The sediment had a water-saturated density of approximately 1.7 t/m^3 (1.2 t/m^3 DM); giving a total of between 1400-2700 tons (800-1600 m^3) of water saturated sediments (900 -1900 tones dry substance), [14].

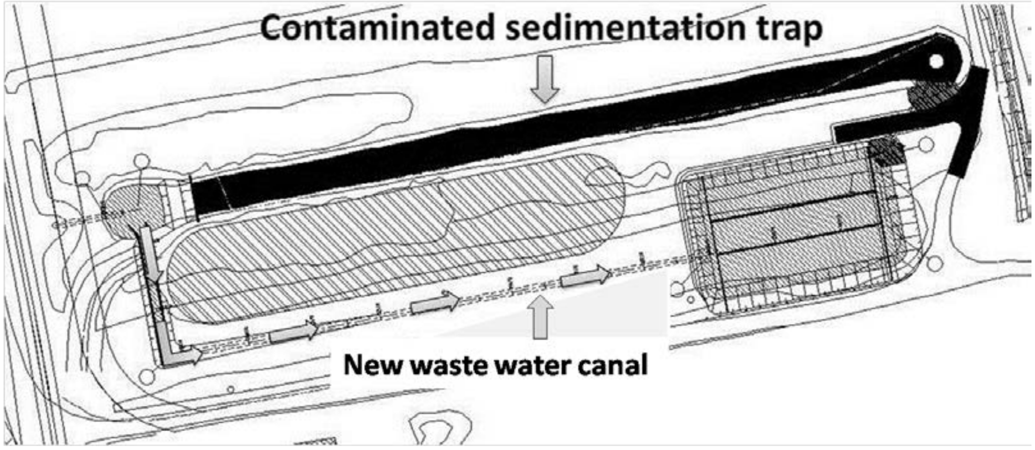

Fig. 4. The outline of the ditch. Since the contamination of the tar was discovered, the water has been led a different path.

The full- scale dredging was carried out in two phases. The freeze plant was placed on the shore and cold brine was conducted to the different freeze plates through a land based distribution system.

Phase 1:

Horizontal PVC hoses (1” c/c 0,2 m), were installed with a specially designed cable plow, at a depth of 0,2 m in the sediments, thereby forming large horizontal volumes of frozen sediment in a shape of frozen plates. The installation was made using a specially designed underwater cable plow mounted on an excavator. The length of each “plate” was 100 m x 1,6 m. After 3-5 days of freezing the material was taken up by using an excavator. The freeze front had progressed between 15 and 25 cm around the hoses. It was thus found that all material had been frozen. During the first phase (4 weeks) about 2200 tones was dredged Figure 5.

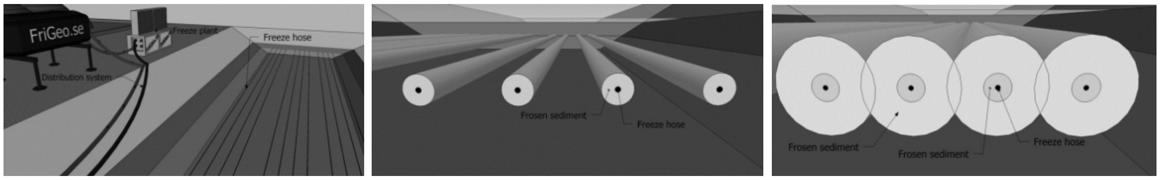

Fig. 5. Schematic view over installation of hoses (left) and the freeze front progression after 1 (middle) and 5 (right) days.

Phase 2: 10 flat freeze plates, with the dimension of 2m x 5m, where used during this phase to freeze the remaining sediments. The lifting, unloading and replacing of freeze-plates were done with an excavator. The freezing cycle varied from 16 to 36 hours, depending on the dredging depth. The thickness of the removed sediment varied from 10 to 25 cm. During the second phase about 300 tones was dredged, figure 6.

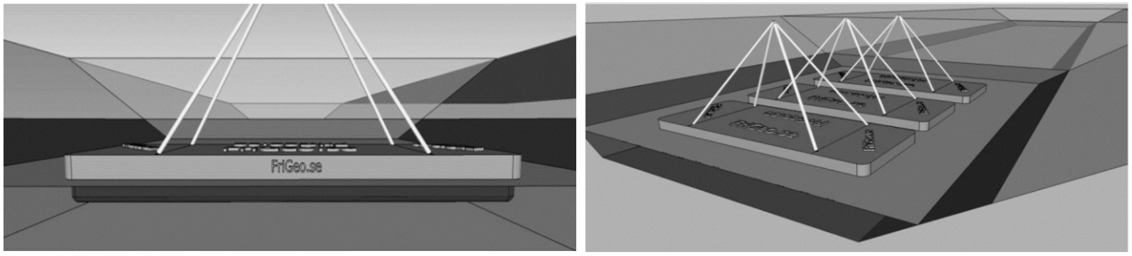

Fig. 6. Schematic view over freeze dredging in phase 2.

The frozen, stabilized material was after uptake loaded on a bed made of geo-membrane and coal. This bed was allowed to thaw and drain away meltwater (dewatering). During the dredging project several heavy rains occurred, but, as the overconsolidation process due to freezing and thawing is irreversible, the rain only wet the material but did not alter the structure back to the volatile slurry form.

The excavated material was then again processed together with the coal in the coking plant. During the process, contaminants are separated in pure form and the waste is transformed to a valuable product.

Freeze sampling

The first freeze corers were designed for sampling from the ice surface [15, 16, 17]. They consisted of cores of metal which were filled with dry ice and alcohol before they were lowered trough the water column down to the sediments. The main problem with the early samplers was that the freezing was uncontrolled and started immediately after the core was filled. An ice layer was formed on the sampler during the lowering trough the water table; this decreased the efficiency and also caused extra disturbance when the sampler penetrated the sediment. The precision of the samplers were also poor causing over or under- penetration. The maximum attainable water depth was at that time 30 m.

Different types of freeze corers have been described [15, 16, 17], used tube-shaped corers; [18] letter-box shaped, and [19] wedge-shaped containers. The thin, wedge shaped type has been found to produce the least disturbance during sediment penetration. Commonly, a mixture of dry ice (solid CO_2) and a liquid with a low freezing point such as alcohol is used as a cooling agent.

To solve the problem of freezing during lowering, presented an improved remotely operated freeze corer, which separated an insulated dry-ice/alcohol container from the freezing wedge. The freezing started after the corer has penetrated the sediment using an electrical pump that circulates chilled alcohol through the wedge. The pump was driven by a 24 V battery which was connected to the sampler by a cable.

Freeze rescue of cold war aircraft in the Baltic Sea

In 1952 a Swedish aircraft of the type DC:3 was shot down by the Soviet Union. The plane was found outside Gotska Sandön in the Baltic Sea and was taken up in 2003-2004. After rescuing the DC:3 Freeze-Dredging was performed in order to retrieve small objects embedded in the sediments spread around in the area close to the aircraft. The water depth was 128 m and the depth of the sediments frozen was 20 cm. The dredging operation was carried out from the Swedish submarine rescue ship Belos. Belos is specially equipped and can keep its position with high accuracy even in very bad weather. The freezing-plant was placed on deck and the cold brine was conducted to the freeze-cells trough 4" and 2" hoses. The freeze cells used were of the flat type with an area of 10 m^2 (5 m x 2m), figure 7. All work under water was carried out with remote operated underwater robots. Originally the plan was to lower 4 cells at each cycle. However due to problems with a lifting beam, only one cell could be lowered at a time. The freezing-time was 16 hours and the average freezing temperature -20 °C. 10 freeze - cycles were carried out in the vicinity of the plane. About 200 m^2 of the sediment with embedded objects were taken up. After uptake the sediment was kept frozen until a careful examination could be made.

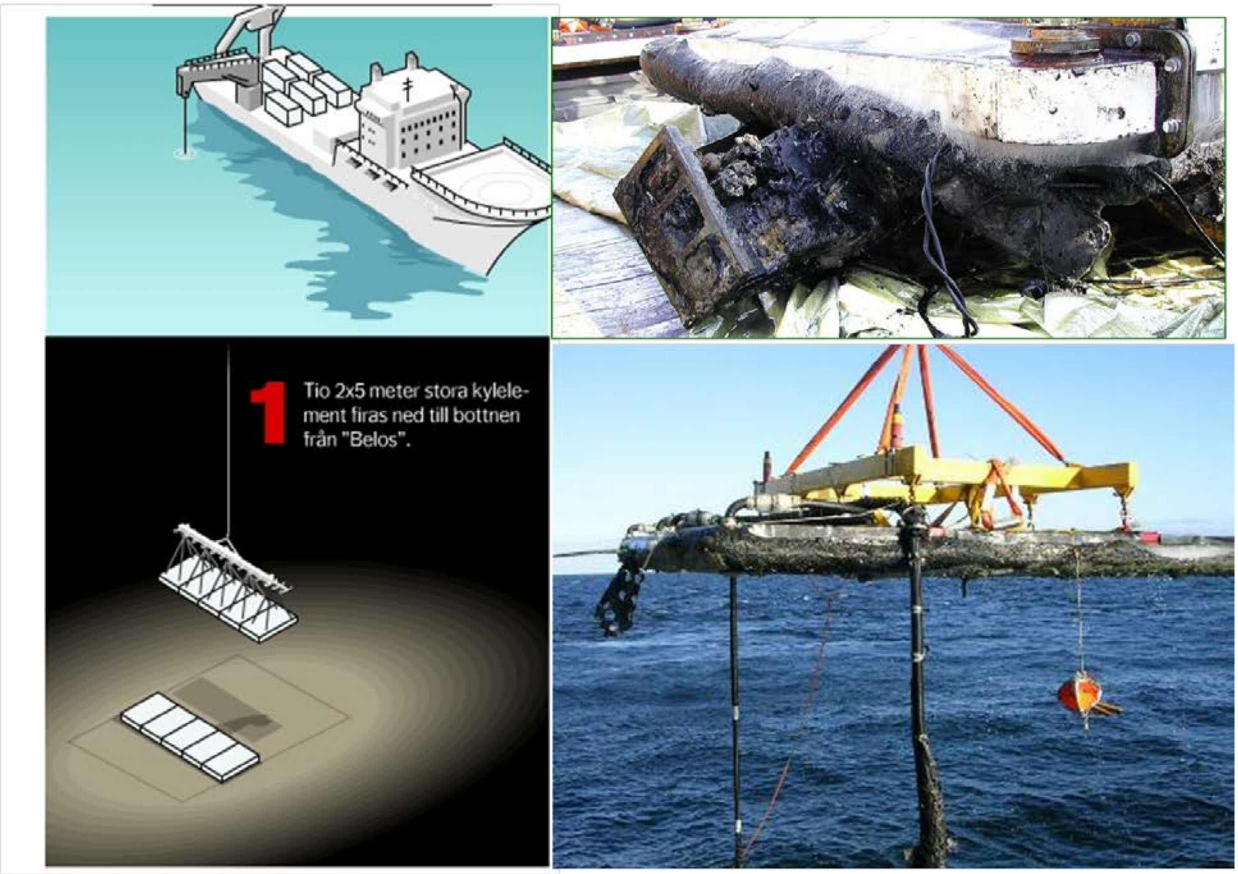

Figure 7. Left; basic design of the dredging system for 130 m depth; top right, salvaged radiotransmittor; bottom right; A freeze- cell breaking the water surface.

Stockholm 2012 – environmental effects

Another large dredging operation was carried out outside Stockholm in 2012. In Stockholm sediments contaminated with heavy metals and PCB was dredged, and transported to landfill in frozen form. During the operation turbidity was measured around the dredging site, figure 8. The measurements showed that;

- Compared to open water conditions turbidity was slightly elevated both inside and outside the silt curtains.
- The turbidity varied unregarding of freeze dredging. The variation could be due to interaction between the silt curtain, wind, waves and currents.
- The turbidity was very low both inside and directly outside the silt curtain. (Mean <5 FNU, occasion =15, n=1900).

Based on the data offered, the environmental authorities concluded that freeze dredging can be made without environmental curtains. Measurements of the dry substance matter in dredged material, and material that had drained on the landfill showed that no extra water was added during uptake and that free drainage of the material reduced the volume by over 50%. The water that drained from the sediments was clear and particle free.

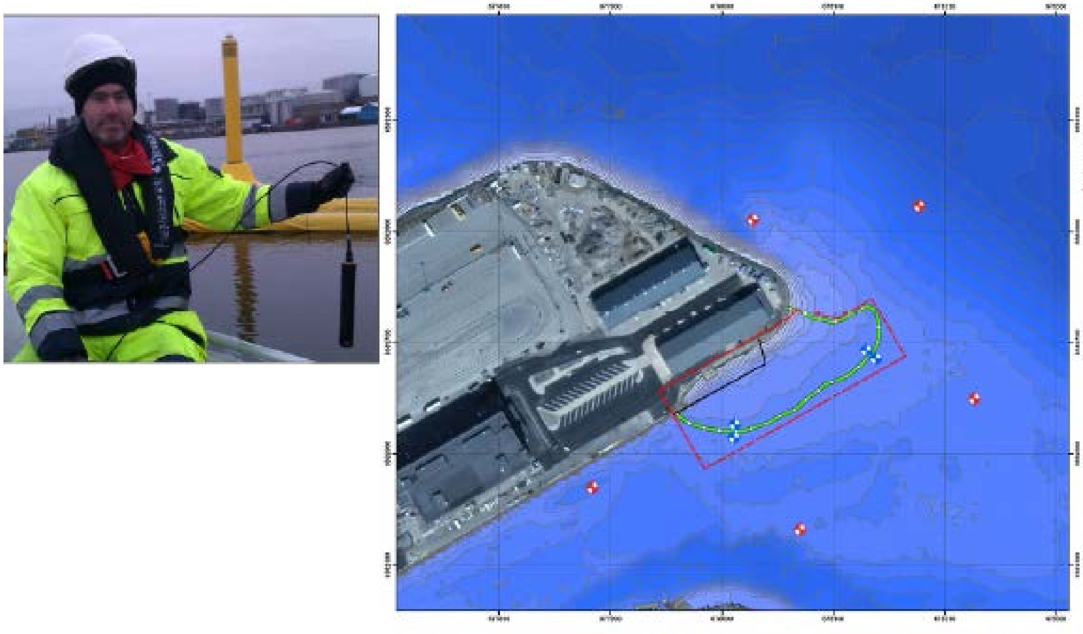

Figure 7. Dredging area and measurement sites for turbidity.

Lessons learned from non-nuclear applications

It is possible to use thermal stabilization also in underwater projects. To minimize energy losses, the refrigeration plant should be placed close to the remediation site. One factor limiting the scale of removal with Freeze-Dredging is the capacity of the refrigeration plant. The water content and thermal properties of the sediment are important for the energy removal needed to freeze the material. The uptake cost for Freeze-Dredging is probably higher than for other environmental dredging techniques but the environmental benefit and post treatment advantages are substantial. Hydraulic dredgers cause low environmental impact during dredging, but add large amounts of water. The added water has to be removed again in the dewatering step. Mechanical dredgers often add little water, but cause environmental impact trough redistribution of sediments during dredging. Even though very little water is added in the uptake process of Freeze-Dredging the freeze-thaw cycle alters the sediment structure causing efficient dewatering without the need for further chemical or mechanical treatment.

In the field tests, both flat freeze-cells as well as cells with vertical pipes and single tubes have been used, all with good results. The uptake of objects from the DC:3 site showed, that it is possible to freeze material at a water depth of almost 130m. With a combination of flat-cells, vertical pipes and single tubes objects embedded in sediments, or placed on the seabed can be rescued using underwater freezing.

APPLICATIONS IN THE NUCLEAR INDUSTRY

In the nuclear industry there are both sediments under water, similar to those outside the nuclear industry, as well as ponds (or spent fuel pools) on nuclear sites that could benefit from the technology described. There are also other industries that may have a radiological contaminated sea bed, such as the oil and gas industry or other NORM industries. Sea, river or bed sediments may be contaminated by radionuclides for several reasons, for example after accidents or controlled releases.

The technology described can basically be applied to the nuclear industry either directly, as for sea beds or after modification and safety assessments.

As freeze sampling is a non-disruptive process it can be applied to sludges in a pond, in order to take a finite volume of sludge without disturbing the rest of the sludge or the sampler can be designed to take samples at a specified depth in the sludge without stirring it up. The sample can then be lifted out of the pond or transferred to a sampling pot elsewhere in the pond.

Another application for freeze sampling is samples from the sea floor, as questions may be asked regarding sediments outside release points, or for mapping if the sea or river bed shall be dredged.

As the nuclear industry has ponds with sludges that sooner or later has to be removed from the ponds, freeze dredging is a possible option as the turbidity is very low during operation. This makes both dredging and object rescue by freezing an option that offers visibility during operation.

Dredging outside the ponds, in sea or river, may also offer advantages with the low turbidity. Another advantage of freeze dredging the sea floor is that only the part of the sediment that contain the radioactivity, which was investigated by the freeze sampling, has to be lifted. The low turbidity means in this case that a much smaller amount of radionuclides will leach into the water and the defined thickness of the lifted sludge means that the amount of waste needing treatment and disposal is limited to the amount containing the radionuclides.

Case study B4

In order to evaluate the processes further a development project has been initiated in Studsvik. The project will contain of the following steps

- Moving the sludgy water to another sedimentation basin
- Re-sedimentation of the sludge after moving
- Freeze sampling of sludge
- Evaluation of radioactive content in the different phases, sludge and thawed water
- Evaluation of treatment options for the sludge
- Evaluation of final waste form and volume reduction factors
- Application to authorities to do the full scale project
- Full scale dredging of sludge
- Waste treatment

Currently the status of the project is that the detailed planning is ongoing and a small modification in the B4-facility is planned in order to totally isolate the sludge from any of the other basins in the building. The timeframe for the project is 12-18 months.

A first set of samples has been taken from the original pool and these samples show that just the freezing of this sludge increases the specific activity in the sludge can be increased by a factor 3-4 by a small amount of drying which means that the water content is 3-4 times lower.

This lab-scale test makes the project very interesting since what is in the balance is the cost for final disposal and the waste form to be disposed of.

CONCLUSIONS AND FUTURE APPLICATIONS

Freeze technology is a well-established alternative to other types of dredging when the sediments that needs to be removed contains materials sensitive to mechanical disturbances, such as PCB, mercury or human remains. As the nuclear industry also have sludges or sediments that would benefit from being removed without disturbance the freezing technology is an option also in this case. Object rescue is also a subject that can benefit from the freezing application, as many pond have small objects in them and digging around in the sludge for them only makes visibility poor and objects hard to find.

During decommissioning of a nuclear site cleaning up the sea floor or river bed outside might also be a demand and in order to minimize the amount of waste freeze dredging may be an alternative to other dredging methods.

PATENTS

Technologies in this paper is covered by patents WO 2011/136732 and WO 2006/098686

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