Removal and re-use of tar-contaminated sediments by freeze-dredging at a coking plant

Luleå, Sweden

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Abstract

Submerged tar-contaminated sediments are generally very loose, which makes remediation challenging. We tested if a modified version of freeze-dredging could be used to remove and dewater such sediments in a canal down-stream a coking plant. PVC hoses carrying a heat medium were placed horizontally in the submerged sediments. Five days of freezing allowed straightforward removal of most of the sediments. Flat freeze cells were placed side by side in the canal to remove the rest. The freeze-thaw process increased the dry substance (DS) content from approximately 50 to 80%. Outdoors storage under rainy conditions did not re-wet the dried sediments. The material was successfully used as feed-stock in the coking plant, with the double cost-benefit of avoided transportation to deposit and reduced use of coal. The study demonstrates that freeze-dredging can facilitate removal, storage and beneficial re-use of submerged tar-contaminated sediments.

Keywords: freeze-thawing, dredging, sustainable management of contaminated sediments

24 Introduction

25 Sediments downstream coking plants are often contaminated with tar as this is a major by-
26 product of the coking process (Harkins et al. 1988). Until recently, tar produced by coking
27 plants was commonly emitted with the wastewater causing severe contamination of receiving
28 waters and soil. So called ‘pump-and-treat’ is a conventional way to remediate tar-
29 contaminated soils and sediments, which in simplified terms means that the sediments are
30 removed by hydraulic pumping and then treated (Kostarelos et al. 2013; Ghosh et al. 1997). A
31 more recent alternative to hydraulic dredging of tar-contaminated sediments is on-site
32 solidification and stabilization (S/S) (Walker et al. 2013). There is evidence that this
33 technique reduces the release of contaminants but the long-term effects of this technique are,
34 however, unclear as the material is left on site and continues to leak, albeit at lower levels.
35 When dredged, the handling of tar-contaminated dredged masses is complicated by the fact
36 that they have a high water content, which makes storage challenging. The two most common
37 approaches are thermal dewatering and mixing with wood chips or other dry products to
38 achieve a higher dry substance (DS) content before incineration or deposition on landfill (US
39 EPA 1994). Both approaches (thermal dewatering and mixing with a dry product) are
40 resource demanding and costly.

41 More recently, ‘freeze-dredging’ has been explored as a way to remove and dewater
42 contaminated sediments (Holm et al. 2013). Pilot studies suggest that this technique has
43 several environmental advantages as it reduces turbidity during dredging, facilitates handling
44 after removal and enables net-energy positive incineration of the end-product, the two latter
45 thanks to efficient dehydration. Freeze-dredging is based on the same principles as artificial
46 ground freezing (AGF), which is a well-established technique first practiced in Wales in 1862
47 (Harris 1995). AGF has been extensively used to stabilize tunnels and excavations and as of
48 late, its application areas have expanded to remediation of contaminated soil (Dash 1991) and

submerged sediments (Holm et al. 2013). In AGF and related technologies, freezing is induced by driving a set of freeze-pipes into the ground, and circulating a refrigerant liquid in the pipes, which is kept at a temperature of -15 to -25 °C by the use of a mobile freeze-plant. When applying AGF for remediation of contaminated submerged sediments, the freeze pipes are arranged in a fashion that enables freezing, lifting and unloading of the frozen material. Previously tested systems have consisted of flat horizontal freeze units for denser sediments and vertical pipes for looser sediments. Neither of these methods is likely to work for extremely loose material such as tar-contaminated sediments from coking plants. The aim of the present study was to investigate if tar-contaminated sediments from a coking plant can be removed by laying out PVC hoses horizontally in the sediment and use them as carriers of heat conducting medium. We discuss how freeze-thawing impacted handling of the material and pros and cons of incinerating the dried tar on site.

Material and Methods

Site description

The study was carried out in the subarctic region of Scandinavia in Luleå, Sweden (65°35'4"N 22°9'14"E), where Swedish Steel AB (SSAB) since 1975 is operating a coking plant. Tar, which is a bi-product of the process, was originally emitted with the wastewater (ca 40 m³ s⁻¹) into a sedimentation canal (ca 230 m x 9 m), which led to Hertsöfjärden, which is an adjacent bay of the Baltic Sea (Figure 1). Over time, the amount of tar in the wastewater successively decreased as more efficient treatment techniques were installed. Investigations carried out by SSAB suggest that the major part of the tar in the canal was emitted in the early 1990s or earlier (pers. comm. Operations Manager on site). In 2001, the wastewater was directed to a new canal with concrete sealed walls and an oil separator dam. There is no water flowing through the old canal, which nowadays is surrounded by dikes. The

bedrock is moraine and the canal sits in sand, which was transported to the location in the early 70s. The level of the standing water in the canal is indirectly determined by the water level of Hertsöfjärden. The bottom of the canal was covered with a ca 0.3 m thick layer consisting of dark and loose sediments with a distinct smell of tar.

Sediment Characteristics

In 2000, the Swedish consultancy firm (MRM) carried out a survey for SSAB collecting samples at four locations using a tube-shaped sediment sampler to a depth of 35-40 cm (MRM 2000). An additional six samples were collected near the shore to a depth of 30-40 cm. In 2004, another Swedish consultancy firm (WSP) carried out a second survey (WSP 2007). This survey included seven soil samples collected with an auger to a depth of 5 m, as well as groundwater samples collected in pipes installed in the holes formed by the auguring. In both surveys, the samples were analysed by GC-MS for polyaromatic hydrocarbons (16 EPA-PAH) and hydrocarbons. The water content of the sediments was in the latter survey determined by drying samples at 70°C and the organic content was determined by loss-on-ignition at 600°C. According to the studies carried out by MRM and WSP, the water content of the sediments was 50%. Only two samples were analysed for organic content and showed a loss-on-ignition of 48% and 82% of DM. The water-saturated density in the samples was determined to be 1.7 t m⁻³ (1.2 t m⁻³ DM); and the amount of sediment was estimated to 1400-2700 metric tonnes (800-1600 m³) of water-saturated sediments (900 -1900 metric tonnes dry substance). The average hydrocarbon content of the sediments was 20 000 mg kg⁻¹ DS (MRM 2000). The average PAH content was 6000 mg kg⁻¹ DS of which 1200 mg kg⁻¹ DS were carcinogenic PAHs. WSP detected di-phenyl-methane in all samples with a highest value of 1200 mg kg⁻¹ DS. They report traces of volatile aromatics, but did not detect chlorinated benzenes or PCBs. The total amount of hydrocarbons in the sediments was estimated to approximately 28 tons of which approximately 8 tons were estimated to be PAHs.

98 **Freezing, Removal and Re-use of Sediments**

99 To freeze-dry the sediments, four one hundred meter long PVC hoses ($\varnothing=1''$) were placed
100 side by side approximately 20 cm below the surface of the sediments, using a custom built
101 underwater cable-plow mounted on an excavator (Figure 2). The hoses were connected to a
102 freezing unit and a refrigerant liquid (-10 to -18°C) was circulated through the hoses, inducing
103 formation of a frozen sediment sheet. The size of each sheet was 100 m x 1.6 m. When
104 frozen, the sheets with the hoses were removed with an excavator. The material was not frozen
105 solid but consolidated to an extent that made it possible to excavate a 20-25 cm thick layer of
106 sediment without difficulty. The frozen sediment was moved from the canal to a bed
107 consisting of geo-membrane and coal (ca 30x80 m, 15 cm thick) and allowed to thaw up to
108 eight days, with thawing time depending on weather conditions.

109 A layer of dark and oily sediments remained at the bottom of the canal. The thickness of the
110 remaining sediment-layer varied from 10 to 25 cm. The dark colour and characteristic smell
111 of the contaminated sediments made it easy to distinguish the border between the
112 contaminated sediments and the underlying sand or moraine. The shallow depth of the
113 remaining sediment made it difficult to reinstall the hose. Instead, the remaining contaminated
114 sediments were removed by placing flat freeze-plates (2 x 5m; Figure 3) side by side in the
115 ditch, using an excavator. Freezing was allowed to continue until the sediments were frozen to
116 the bottom of the ditch (Table 1). The plates with frozen sediment cakes were moved from the
117 canal to the geo-membrane bed where the frozen material was removed from the freeze-plates
118 and allowed to thaw. The drainage water from both runs was returned to the sedimentation
119 canal. The thawed material was successively moved to the coking facility's coal storage site.
120 The dried material was mixed with coal and used as fuel in the coking plant.

Results and discussion

Removal

As the refrigeration fluid was allowed to circulate in the horizontally placed hoses, the freeze front progressed evenly around the hoses, suggesting that the sediment acted as an insulating layer, thus facilitating the freezing process. After 3-4 days, the freeze-front had progressed 15-25 cm from the hoses and came to a halt after about five days. Approximately 2200 tons of sediment was removed in this phase (Table 1).

The freeze-front progression around the hoses was slower than expected from theoretical calculations made with the modified Berggren equation (Andersland & Ladanyi 1994) (Rostmark 2004). Thermally induced ground water flow is a possible explanation for the slower than expected freezing speed, as this would cause convective heat transfer in the material or ice lens formation. It is also possible that the high content of hydrocarbons in combination with dissolved organic compounds and ions caused freeze-front depressions in the material.

When the freeze-plates were placed on top of the remaining sediments, it took 16 to 36 hours for the freezing front to move from the plates to the bottom of the canal, with the freezing time clearly increasing with the thickness of the sediments. Approximately 300 metric tonnes were removed during this second phase (Table 1).

The total amount of sediments that were removed was thus 2500 metric tonnes wet material, which was within the span previously estimated by the consultancy firms (1400-2700 metric tonnes) and resulted in 1600-1700 metric tonnes dried material.

Dewatering

The thawed material reached a hard and rock-like structure with a dry matter content of approximately 80% (n=27, s.d. 9.0). Freeze-thawing of heterogeneous materials is a complicated process being a combination 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 (Harris 1995). A number of authors have stated that a necessary prerequisite to obtain an effective improvement in sludge dewatering potential is a low freezing rate; the low freezing velocity starts up a freezing mechanism called “gross-migration” first reported by (Logsdon & Edgerley 1971). In contrast, when the freezing rate is high, particles in the solution are trapped in the developing ice layer resulting in little or no improvement of the dewatering potential. Already in 1962, Corte showed that fine particles migrate under a wide range of freezing rates and coarse particles migrate only at low freezing rates (Corte 1962). This means that large particles are more likely to be trapped in the advancing ice front compared to the smaller particles. The efficiency of the process depends on factors such as the mineralogical composition, size and shape of the particles, permeability, freezing conditions i.e. initial soil temperature, thermal properties, freezing temperatures, energy removal rate and the amount of dissolved organic matter, solids and cations, (e.g. Andersland & Ladanyi 1994; Knutsson 1997; Martel 2000; Örmeci & Vesilind 2001).

It is more challenging to dry organic rich sediments such as tar-contaminated sediments than sediments with a low organic content as a larger part of the water is bound and superficial water (Palermo 2010). The fact that the material reached a DS content of 80% shows that the freezing speed was sufficiently slow to allow the water crystals to grow without incorporating other material, thus causing the bound water to separate from the tar and other particles.

Handling after removal

A number of heavy rains occurred during the dewatering phase but the material did not return to its former slurry-like consistency. This infers that the physic-chemical properties of the material had changed during the freezing process, as described by Vesilind and Martel (1990). Using their terminology, “free” water is not associated with aggregates and is easily removed with conventional mechanical dewatering systems. “Interstitial” water is trapped inside an aggregate or held by capillary forces and a mechanical dewatering device can break the aggregate and free the interstitial water. “Surface” water is connected to particles by superficial forces and mechanical systems can also remove this type of water. The fourth type of water, which is called “bond” water (chemically bound to the particles), can only be released from particles with thermal or chemical treatment. Removal of bond water causes structural changes at the molecular level, which hinders rewetting of the material.

Pros and cons of incinerating the dried material

The dried sediments were mixed with coal and used as feed-stock in the coking plant. In a coking plant, the coal is heated in narrow, airtight ovens until it is in an almost flowing, plastic form and some of the material is gasified (above 1000°C) and the coal is converted to 75 percent coke and 25 percent gas. The gas is cleaned in several steps and the cleaned gas is generally the major product. In addition, various raw materials are recovered for the chemical process industry, such as fertilizers for agriculture, naphthalene, sulfur, ammonia and benzene, and various products used by manufacturers of perfumes and pharmaceuticals. and the high DS content rendered net-energy positive incineration. According to the operational staff, the introduction of the recovered material did not interfere with the processes in the sensitive system (Börje Sikblad SSAB, pers. comm.). The dried sediments were thus beneficially used as feed-stock, replacing coal. The exact amount of coal that the sediment replaced was not determined but a rough ‘guesstimate’ gives that the dried

sediments replaced approximately 1000 metric tonnes of coal, based on the fact that the energy value of tar is approximately twice that of coal (ca 15-27 GJ ton⁻¹, vs ca 36 GJ ton⁻¹) and assuming that the energy value of the sediment was about half of that of tar.

In summary, the process as a whole gave cost-savings in several ways: dewatering reduced the bulk material that needed to be handled and thus reducing on-site transportation costs. Incineration on-site led to that off-site treatment was avoided, which costs about \$500US per metric tonne (not including transportation). Also, the tar-contaminated sediments replaced coal as feed-stock in the coking process, thus reducing the feed-stock cost. The present study cannot be used to carry out a full cost-benefit analysis, as this requires more careful recording of the costs involved.

Conclusions

The present full-scale study demonstrates that horizontally installed hoses can be used to excavate loose sediments with a low DS content. The study also shows that the technique can be used to efficiently dewater the sediments to a high DS content and that it is possible to beneficially reuse the dredged material when it has a high organic content. The study shows that hoses placed horizontally in the sediments followed by the use of flat cells can facilitate removal of contaminated sediments. The consolidating effect induced by the horizontal PVC-hoses indicates that repeated freeze-thaw cycles *in situ* would have induced consolidation to the bottom of the canal, suggesting that it would be possible to excavate all of the contaminated material without the additional use of flat cells.

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References

- Andersland, O.B. & Ladanyi, B., 1994. *An introduction to frozen ground engineering*, New York: Chapman & Hall.
- Corte, A.E., 1962. Vertical Migration of Particles in Front of a Moving Freezing Plane. *Journal of Geophysical Research*, 67(3), pp.1085–&.
- Dash, J.G., 1991. Ice technology for hazardous waste management. *Waste Management*, 11, pp.181–189.
- Ghosh, R.S., Saigal, S. & Dzombak, D.A., 1997. Assessment of in situ Solvent Extraction with Interrupted Pumping for Remediation of Subsurface Coal Tar Contamination. *Water Environment Research*, 69(3), pp.295–304.
- Harkins, S.M. et al., 1988. *US production of manufactured gases: Assessment of past disposal practices*, Environmental Protection Agency, Cincinnati, OH.
- Harris, J.S., 1995. *Ground freezing in practice*, London, UK: Thomas Telford Publishing.
- Holm, G., Lundberg, K. & Svedberg, B., 2013. Sustainable Management of Contaminated Sediments, In: *Proceedings of the 18th Conference on Soil Mechanics and Technical Engineering, Paris 2013*. pp. 3215-3218
- Knutsson, S. ed., 1997. General thermomechanical model of freezing soil with numerical application. In: *Proceedings of the International Symposium on Ground Freezing and Frost Action in Soils*. Rotterdam, pp. 101–105.
- Kostarelos, K., Yoon, S. & Lee, K.Y., 2013. Coal tar recovery using enhanced “pump-and- treat.” *Journal of Chemical Technology and Biotechnology*, 88(12), pp.2252–2263.
- Logsdon, G.S. & Edgerley, E., 1971. Sludge Dewatering by Freezing. *Journal American Water Works Association*, 63(11), pp.734–&.
- Martel, C.J., 2000. Influence of dissolved solids on the mechanism of freeze–thaw conditioning. *Water Research*, 34(2), pp.657–662.
- MRM, 2000. *Provtagning och analys av sediment i koksverksdike och Hertsöfjärden – Luleå. För SSAB, MRAP 0001*.
<http://www.ssab.com/global/documents/environment/bilaga%20d%20mkb%20med%20bilagor%20081104.pdf>
- Örmeci, B. & Vesilind, P.A., 2001. Effect of dissolved organic material and cations on freeze-thaw conditioning of activated and alum sludges. *Water Research*, 35(18), pp.4299–4306.
- Palermo, L., 2010. In situ and bioremediation of organic pollutants in aquatic sediments. *Journal of Hazardous Materials*, 177, pp.81–89.
- Rostmark, S., 2004. *Frysmuddringsteknik för sanering av förorenade sedimentområden*. Luleå tekniska universitet, Luleå. Luleå University of Technology, Licentiate thesis. Nr

2004-77

US EPA. 1994. *ARCS Remediation Guidance Document*. EPA 905-B94-003. Chicago, Ill.: Great Lakes National Program Office. <http://www.epa.gov/greatlakes/arcs/EPA-905-B94-003/B94-003.ch7.html>

Vesilind, P.A. & Martel, C.J., 1990. Freezing of water and wastewater sludges. *Journal of Environmental Engineering*, 116, pp.854–862.

Walker, T.R. et al., 2013. Monitoring effects of remediation on natural sediment recovery in Sydney Harbour, Nova Scotia. *Environmental Monitoring and Assessment*, 185(10), pp.8089–8107.

WSP, 2007. *Koksverksdiket*, Luleå: SSAB Tunnpå AB, Luleå.

Table 1. Overview of the different steps in the freeze-dredging procedure used to remove tar-contaminated sediments downstream a coking plant in northern Sweden.

Step	Time (hrs)	Removed Sediment		Dewatered Sediment	
		Mass (metric tonnes)	Dry matter (%)	Mass (metric tonnes)	Dry matter (%)
Removal of top layer		Ca 2200	50	Ca 1375	80
Placement of hoses	64				
Freezing	48-120				
Removal	23				
Removal of bottom layer		Ca 300	50	Ca 190	80
Placement of freeze-plates	24				
Freezing	24-72				
Removal and transport to thawing storage	48				
Thawing	24-38				
Transport to feed-stock storage	4

Figure 1. Map over study site: old sedimentation canal etc at coking plant outside Luleå, Sweden ($65^{\circ}35'4''\text{N}$ $22^{\circ}9'14''\text{E}$). Tar from the canal was removed by freeze-dredging, thawed on-site and fed into the coking plant as fuel.

Figure 2. Schematic overview of freeze-dredging design for removal of tar-contaminated sediments from coking plant, Lulea, Sweden using horizontally installed PVC hoses with a refrigerant liquid as carrier (left image). Mid image and image to the right illustrate progression of the freeze-front in the sediment.

Figure 3. Schematic overview of freeze-dredging design for removal of remaining tar-contaminated sediments from a coking plant, Lulea, Sweden using freeze-plates to remove sediments remaining at the bottom of a canal.