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Use of cement and quicklime to accelerate ripening and immobilize contaminated dredging sludge

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Abstract

In this study cement and quicklime are examined as binders to enhance the ripening process and immobilize contaminants in dredging sludge. Ripening comprises the drying in the open air till a dry matter content of 50–55% is reached. For this study, a dredging sludge of the highest contamination category was used. The binders speed up the ripening process substantially since the binders as such increase the dry matter content upon mixing, but they also modify the structure so that evaporation is facilitated. Furthermore, the reaction of cement and quicklime with water generates heat that also stimulates evaporation, and both binders, in combination with dredging sludge, bind water chemically (twice as much as expected). The total time for ripening could be reduced by 70%, which means that existing treatment depots can be used more effectively. The emission of contaminants was determined by a standard leaching test. The cement and quicklime had opposite effects on the leaching of constituents. The addition of cement had negative effects on sulphate, fluoride, and zinc, which were compensated by the addition of quicklime. On the other hand, cement reduced the emission of chloride, copper, and nickel, while quicklime seemed to increase the emission of these constituents. The concentration and emission of contaminants of the treated dredging sludge meet the requirements of the current legislation. It is therefore concluded that the presented method is able to produce, in a much shorter time, an applicable building material from contaminated dredging sludge.

Keywords: Sludge; Cement; Quicklime; Ripening; Leaching

1. Introduction

The Netherlands is situated in the delta of the rivers Rhine, Meuse and Scheldt. A large part of the sediment transported by these rivers settles in this delta. For shipping and a safe discharge of the water it is necessary to dredge the Dutch waterways regularly, as is also the case in many other river deltas worldwide. In the 1980s it became clear that a large part of the dredged sludge was contaminated due to discharges of industrial and domestic waste water, shipping, agriculture, and other non-point sources. Because of the high costs associated with removing contaminated sludge, organizational bottlenecks, and the lack of suitable destinations of the sludge, the dredging of Dutch waterways lags behind. Consequences of this are an increased risk of economical damage, e.g. through floods and reduced accessibility of harbors, and the possibility for ecological damage. The estimated amount to be dredged in the Netherlands in the period 2002–2011 is about 400 billion m^3 of which half, 195 billion m^3, is from fresh waters [1]. Of this fresh water dredging sludge approximately 75 billion m^3 is heavily polluted, which corresponds to almost 40%.

The clean or slightly contaminated sludge is allowed to be spread over land or surface water. This is done with only 30% of the total amount of fresh water dredging sludge, the remaining part cannot be spread because of high contamination levels or limited space along the waterways. This large amount of dredging sludge needs to be treated or disposed. The Dutch policy [2,3] aims at the treatment of at least 20% of the contaminated dredging sludge such that it can be reused.

The most common technique at this moment is ripening. Ripening of sludge is the natural process where the sludge is transformed by drying and oxidation from a wet substance into a soil like material. In this technique, after dredging the sludge is transported to an open air depot. The dredging sludge arrives

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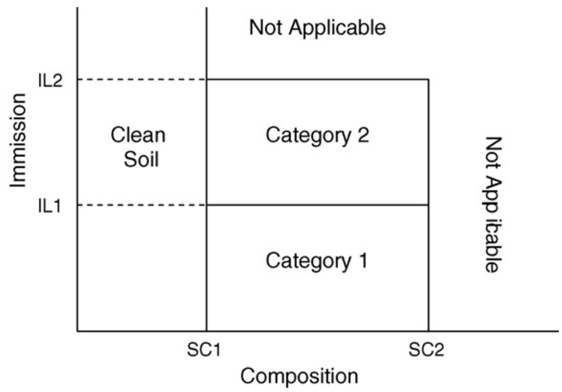

Fig. 1. Classification of soil for the applicability as building material (SC, standard composition; IL, immission level).

at the depot with a dry matter content of 20–25%. This material has no mechanical bearing capacity and is as such not applicable. The sludge is stored in layers of up to 1 m, a drainage system at the bottom facilitates the discharge of rain and excess of water in the sludge. When the sludge reaches a dry matter content of 35–40% the aerobic conditions for biological activity are reached initiating the oxidation process. In the Netherlands this process only takes place between April and October when the temperatures are high enough. To enhance the oxidation process and evaporation the dredging sludge is turned over two to three times a year. Only when a dry matter content of 50–55% is reached the product can be deployed as building material in civil constructions (e.g. as road base material). In the current practice this could take 1.5–2 years. As a result of this long handling time and the limited storage capacity it is impossible to keep up with the supply of dredging sludge. This points out the need for alternative treatment methods that reduce the handling time.

Another problem with the reuse of dredging sludge is the level of contamination. Before the dredging sludge can be applied it needs to fulfill stringent requirements. In the Netherlands four categories for soil as building material are distinguished [4]: Clean Soil, Category 1 or 2, and Not Applicable (see Fig. 1). Building material is classified as Clean Soil when the concentrations (in mg/kg) of all contaminants are below the standard composition SC1. This material contains little to no contaminants and can be applied without any problem. When the concentration of at least one of the contaminants exceeds SC1 but is still lower than SC2 the material is classified as Category 1 or 2. The difference between Category 1 and 2 is determined by the amount of contaminants released from the material during a prescribed leaching test. From this test the immission, i.e. the amount of contaminants received by the environment, can be calculated. For Category 1 the immissions (in mg/m^2) of all contaminants is below immission level IL1. This material can be applied without any additional measures. Category 2 material has an immission between IL1 and IL2 and can only be applied when additional measures are taken to reduce the emission to the environment. When IL2 or SC2 are exceeded the material is classified as Not Applicable and should be disposed. The current ripening procedure usually changes the dredging sludge into a Category 2 material. Since in February 2004 the requirements for some contaminants have been relaxed more material satisfies the requirements for Category 1.

The application of the treated sludge also depends on the mineral composition. Sludge with high clay content will mainly be applied as filling material or in traffic noise barriers. When the sludge consists of mainly sand, the materials could also be applied as subgrade. Besides avoiding permanent storage of contaminated dredging sludge, making dredging sludge applicable as building material also contributes in solving the shortage in raw material.

Objective of this research is to find an alternative method to reduce the treatment time for contaminated dredging sludge by ripening and to reduce leaching (immobilization) such that a stable product is obtained that can be applied as building material.

2. Previous research

The long time required for ripening has initiated various studies to find ways of accelerating the ripening process. One option to accelerate ripening is by electrochemical treatment [5]. In this method an electrical current is transmitted through the sludge. This method reduced the ripening time with a factor two. However, the investment and energy costs are high for this method. Another method is supplying heat. In a study by NOBIS [6] it was shown that ripening of dredging sludge proceeded twice as fast when the temperature was increased by 5 °C. In winter a larger temperature difference was necessary. By using a closed system with a heat exchanger the energy consumption could be minimized. In another study hot steel balls were used to dry the sludge [7]. By mixing 125 metric tonnes of steel balls with a diameter of 12 mm and a temperature of 120 °C, 2 metric tonnes of dredging sludge could be treated in 1 h from a dry matter content of 50% to a dry matter content of 90%. Disadvantages of this procedure are the high investment costs, high-energy consumption, and noise pollution produced by the steel balls. Besides this, the dredging sludge already needs to have a dry matter content of 50% prior to the treatment. Pinto et al. [8] treated storm water runoff solid residuals with the binders Portland cement, quicklime and sodium bentonite, and studied the early age (up to 40 h) hydration.

In the Netherlands different studies have evaluated the addition of cement to dredging sludge in order to immobilize/stabilize contaminants. The objective of most of these studies was to obtain a shaped building material [9]. A building material is considered to be shaped if it has a volume of at least 50 cm^3 and a durable consistency under normal conditions [4]. A study in Singapore considered the application of dredging sludge in the shaped products brick and concrete [10]. For the production of brick 30–40% dried sludge in combination with clay was used. For concrete only up to 10% sludge was added to guarantee the strength and to prevent the concrete from cracking and absorption of moist. In France a study was performed on the immobilization of dredging sludge by adding cement and fly ash [11]. In Spain the same was done with sludge from a waste water treatment plant [12]. Here a mix was made consisting of 25–35% sludge in combination with 65–75% cement and/or fly

Table 1
Particle size distribution of the mineral fraction of the used dredging sludge

Fraction	Size (μm)	Mass fraction (%)	Cumulative larger (%)
Clay	<2	22.0	100
Silt	2–16	15.0	78.0
	16–63	34.0	63.0
Sand	63–90	1.1	29.0
	90–125	1.3	27.9
	125–180	2.3	26.6
	180–250	3.3	24.3
	250–355	4.7	21.0
	355–500	4.2	16.3
	500–1000	5.4	12.1
	1000–2000	6.7	6.7
Gravel	>2000	0	0

Table 2
Chemical composition of the mineral fraction of the used dredging sludge and of cement

Mineral	Symbol	Mass (%) sludge	Mass (%) cement
Silicate	SiO_2	58.3	28.4
Aluminum oxide	$A1_2O_3$	8.8	13.1
Iron oxide	Fe_2O_3	3.6	1.24
Calcium oxide	CaO	14.7	42.8
Magnesium oxide	MgO	2.6	–
Sodium oxide	Na_2O	1.3	0.33
Potassium oxide	K_2O	1.5	0.6
Titanium oxide	TiO_2	0.5	–
Phosphorus oxide	P_2O_5	0.3	–
Sulphate	SO_3	2.2	3.47
Chloride	Cl^-	0.1	0.033
Manganese oxide	MnO_2	0.2	–
Zinc oxide	ZnO	0.09	–
Copper oxide	CuO	0.01	–
Lead oxide	PbO	0.04	–
Rubidium oxide	Rb_2O	0.01	–
Strontium oxide	SrO	0.04	–
Zirconium oxide	ZrO_2	0.03	–
Total		96.9	90.0

ash. The slow reaction was solved by adding calcium chloride. The mixtures easily reached a pH of 13, which has negative consequences for the emission of contaminants like sulphate. This could be explained by the high quantities of cement added.

This study will address the treatment of dredging sludge with binders such that under normal atmospheric conditions the time required for ripening is reduced and the product can be used as a non-shaped (granular) building material. This will avoid high investment costs and high-energy consumption. Moreover, it is expected that through addition and binding of the binders both the dry matter content will increase faster and leaching of contaminants is reduced.

3. Materials and methods

3.1. Dredging sludge characteristics

In the Netherlands the contamination level of dredging sludge is divided into five classes, Class 0 being the cleanest, Class 4 being the most contaminated. In this study Class 4 dredging sludge was used to assess the effect of the binders on the different contaminants. The used dredging sludge came from urban waters in the city of Arnhem, The Netherlands.

The studied dredging sludge contains 13.6% organic matter, determined by loss on ignition at 550 °C. The loss on ignition at 1200 °C was 18.9%. The particle size distribution of the mineral fraction of the dredging sludge was determined by sieving and the pipet method for fractions smaller than 63 μm [13]. Table 1 shows the results of the particle size analysis. Table 2 shows the oxide composition of the dredging sludge determined by X-ray fluorescence spectrometry (XRF). Using X-ray diffractometry (XRD), it appeared that a significant part of the minerals is crystalline (58% quartz, 12% calcite), the remaining part most likely contains amorphous material.

3.2. Ripening experiment

As binders to accelerate ripening cement and quicklime (CaO) were chosen. Both binders bind moisture, an excellent quality to make the sludge applicable as building material. The oxide composition of the cement is included in Table 2 as well. In some preliminary experiments [14] it was determined when (at which dry matter content) and how much of the binders should be added and what the most representative atmospheric condition is. To avoid high costs, it is preferred not to add too much cement and/or quicklime. Large amounts of these binders would also increase the pH of the materials too much. The amount of cement added varies between 0 (reference) and 15% of the weight of the dredging sludge. Quicklime is added to improve the structure and bind metal ions. From the literature it appears that 0.5–1% quicklime is sufficient to obtain a desired effect [15].

In the trial experiments the binders were mixed into the dredging sludge at different dry matter contents. In the samples where the binders were mixed in with the sludge with dry matter content of 27%, pieces of hardened cement were found at the bottom of containers after the experiment. This indicates that the water content was too high and that the cement was leached out and reacted only with water instead of binding to the sludge. The water content should not be too low either because this would increase the untreated storage time of the sludge in the depots. The most ideal dry matter content of the sludge at which the binders should be added, turns out to be about 35%.

The ambient relative humidity in the laboratory is about 25%, which implies that the samples would dry unrealistically fast compared to normal atmospheric conditions. Accordingly, the containers were placed next to each other alternated with some containers filled with water and covered by a large plastic. The relative humidity was regulated with plastic flaps and maintained at a value of around 70% (see Fig. 2). The temperature in the laboratory was 23–24 °C. The conditions created are therefore representative for summer conditions.

Round containers with a diameter of 40 cm were filled with 10 cm of sand and 20 cm dredging sludge on top of it. A drainage

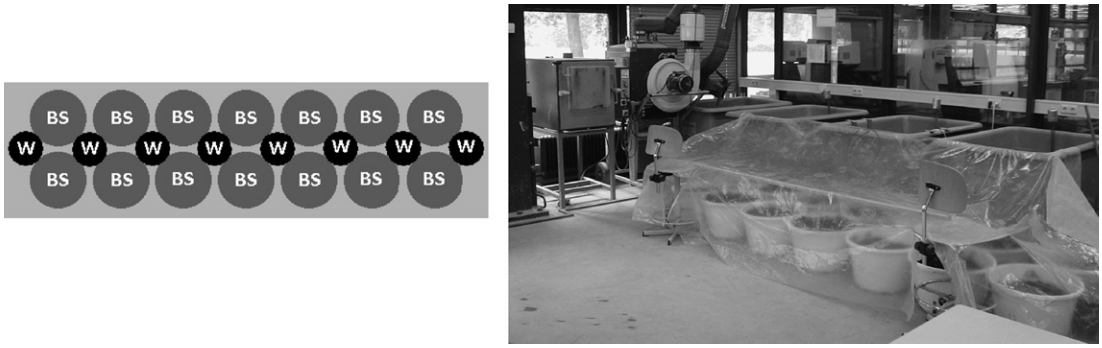

Fig. 2. Set-up of the ripening experiment (BS, containers with dredging sludge; W, containers with water).

system of pipes was not necessary because at a dry matter content of 35% the sludge contains a little or no water that can drain freely, as most of the water is bound by capillary forces. Prior, during and after the experiment several parameters were monitored such as mass, dry matter content, temperature and humidity.

The initial dry matter content of the original sludge was 39%, which was lowered to 35% by adding water. The sludge in the containers was mixed with different amounts of binders: no binders (reference), 7% cement and 0.5% quicklime, 14% cement and 1% quicklime, and 15% cement only (mass% based on mass wet sludge), and an admixture. Except for the last one, each combination was carried out with and without regular mixing. All experiments were carried out in duplicate. In Table 3 the composition of the samples is given. The first number of the code of the sample gives the percentage of cement, the second the percentage of quicklime and the third indicates whether the sample was regularly mixed (1) or not (0).

At $t = 0$ the binders were mixed into the samples by hand, and after 2 weeks, at $t = 2$, was started with mixing the samples X/X/l. This was repeated every 2 weeks until week 12, always done by hand. This became more difficult in time when more binder was mixed in, that is the reason why the mix with 15% was not regularly turned. The last measurements were done after 20 weeks. After this, subsamples were taken to do leaching tests.

3.3. Leaching test

An important criterion for the application of treated dredging sludge as building material is the release of contaminants. The emission and subsequent immission of contaminated material is determined by a leaching test. The immission levels that determine the applicability of the material are given in the Building Materials Decree [4]. To analyze the effect of ripening (with and without binders), leaching tests were performed on the original dredging sludge and after the ripening experiments.

The leaching test simulates the leaching of contaminants from granular materials in an aerobic environment. In this study the leaching test was carried out according to NEN 7343 as prescribed by the Dutch regulations [4]. For this test a vertical column with an inner diameter of 5 ± 0.5 cm is packed with 0.5 kg of the sample and flushed with different liquid to solid ratios (L/S) varying from 0.1 up to 10 l leaching liquid per kg dry matter. The percolating liquid consists of de-ionized water acidified with a small amount of nitric acid to a pH of 4 ± 0.1 to simulate acid rain water and is pushed against gravity through the column. The sample is first flushed with 0.05 l of percolating liquid (L/S = 0.1). This fraction is collected and filled up to 0.1 l for the second fraction (L/S = 0.2). The second fraction is flushed through the column and collected again. This process is repeated with L/S fractions 0.5, 1, 2, 5, and finally 10 with a total of 5.0 l (V_i) leaching solution per kg dry matter. Here, only the cumulative fraction L/S = 10 was analyzed, whereby the sludge sample was 0.5 kg. From this the emission of individual contaminants ($E(\text{L/S} = 10)_i$) is calculated, and subsequently the maximum height (h) pertaining to the emission of each contaminant [14].

4. Drying results

4.1. Drying

The evaporation of water was determined by measuring the weight of the (duplicate) samples biweekly. The difference

Table 3
Composition of the samples for the ripening experiment (mass in kg), dm is dry matter content

	Binder	Mixed	Sludge	Water	Cement	Quicklime	dm (%)
0/0/0	None	No	27	3	0	0	35.0
0/0/1		Yes	27	3	0	0	35.0
7/0.5/0	7% cement	No	27	3	2.1	0.15	39.6
7/0.5/1	0.5% quicklime	Yes	27	3	2.1	0.15	39.6
14/1/0	14% cement	No	27	3	4.2	0.3	43.5
14/1/1	1% quicklime	Yes	27	3	4.2	0.3	43.5
15/0/0	15% cement	No	27	3	4.5	0	43.5

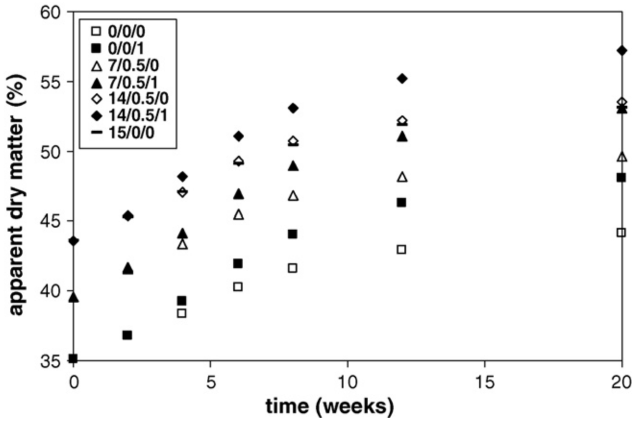

Fig. 3. Apparent dry matter content (%) vs. time (weeks) based on mass loss due to evaporation.

between the measured mass and the mass at $t = 0$ equals the mass lost by evaporation. Based on the original dry mass content (dm) and the mass loss due to evaporation the apparent dry matter content could be calculated. In Fig. 3 the dry matter content is given as a function of time. The depicted values are the mean averages of the duplicates. The maximum difference between the duplicates after 20 weeks turned out to be smaller than ± 0.2%.

The initial values at $t = 0$ correspond to the last column of Table 3. The samples in which binders are mixed start with higher dry matter contents because the binders add to the dry matter content. From Fig. 3 it can be seen that the mixed samples have a larger increase in dry matter content than the samples that are not mixed. After 20 weeks the mixed samples have a dry matter content that is of about 3–4% higher compared to the unmixed ones. Regular mixing improves the aeration and enhances the evaporation of water and as such has a positive effect on the dry matter content of the sludge. Fig. 3 also reveals that, when the increase in dry matter is accounted for, the addition of cement and quicklime slightly enhances the loss of water by evaporation. Cement, and in particular quicklime, improve the structure of the sludge and hence the aeration. In Fig. 4 the change in dry matter content determined by drying at 105 °C is given. As in Fig. 3, the dry matter content increases faster for samples that are regularly

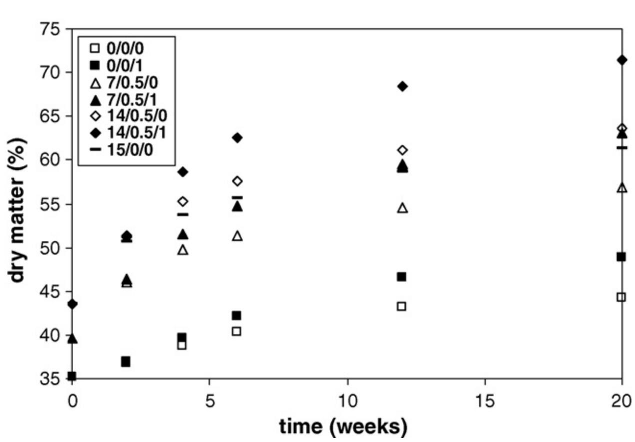

Fig. 4. Actual dry matter content (%) vs. time (weeks) based on drying at 105 °C.

mixed and that include binders. Since cement reacts with water part of the water will become chemically bound. This water will not evaporate at 105 °C, consequently the dry matter content is higher than the apparent dry matter content based on mass loss, given in Fig. 3. To examine and validate this effect, the apparent dry matter was compared with the dry matter for (both the mixed and unmixed) dredging sludge that is not mixed with binders (untreated). In these two cases it appeared indeed that the dry matter computed by the evaporated water (mass loss) corresponds within a few % with the dry matter obtained by drying at 105 °C.

Fig. 4 shows similar trends as in Fig. 3, only the effects of cement and quicklime are more pronounced. Besides the advantage of accelerated drying and an additional increase in dry matter content due to chemically bound water the samples with binders already start with a higher dry matter content. Samples with 7.5% binders have a time advantage compared to samples without binder of about 4 weeks. The samples with 15% binder gain 8 weeks by the addition and corresponding dry matter increase. Moreover, in the first 4 weeks the dry matter content of the samples with binders increases faster than the samples without binder. This is mainly caused by the reactions of cement and quicklime with water. After 4 weeks this reaction is more or less completed and the dry matter content increases at a similar rate as the samples without binder. As said, the dry matter content of the dredging sludge should be at least 50–55% before it is applicable as building material. Based on extrapolation, the samples without binder reach a dry matter content of 50% after approximately 26 (mixed) or 60 (not mixed) weeks. For the mixed sample with 7.5% binders this is already reached within 4 weeks. This includes the time benefit gained by mixing in the binders. When it is assumed that after the dredging sludge is deposited, 8 weeks are required to obtain a dry matter content of 35% and that then the binders can be mixed in, this means that the treatment time in the depots is reduced by about 65%. For the samples with 14 and 15% binders the total treatment time is even reduced by about 70%.

The acceleration of the ripening process by mixing binders with the dredging sludge means that in the same time span, three times more dredging sludge can be treated compared to the current practice.

4.2. Water binding

From the previous section it became apparent that the reaction of cement and quicklime with water increased the dry matter content. The cement reacts with water and retains this water even after drying at 105 °C. From the literature [16] it is known that after complete hydration, 100 g cement is able to retain about 40 g of water, of which 15 g is physically bound water that evaporates after drying at 105 °C. The other 25 g of the water is chemically bound and does not evaporate at 105 °C (so called non-evaporable water).

This was verified in a few basic experiments in which 25, 50, and 75 g of cement were mixed with 325 g of water to obtain water/cement ratios of 13, 6.5 and 4.3, respectively. These values are very high but similar to the water/cement ratios in the

Table 4
Chemically bound water expressed as % of added mass of binder in mix as a function of time (weeks)

Code	wcf[a]	$t=2$	$t=4$	$t=12$	$t=20$
1	13	24.4%	25.2%		
2	6.5	24.0%	25.4%		
3	4.3	24.9%	24.8%		
7/0.5/0	9.3	60.7%	82.4%	74.0%	82.6%
7/0.5/1	9.3	62.8%	96.1%	94.4%	107.6%
14/1/0	4.6	41.4%	57.4%	56.4%	62.6%
14/1/1	4.6	42.9%	71.7%	78.8%	82.3%
15/0/0	4.3	38.8%	46.1%	43.6%	51.5%

Codes 1, 2 and 3 reflect experiments with cement only.
[a] wcf, water cement factor.

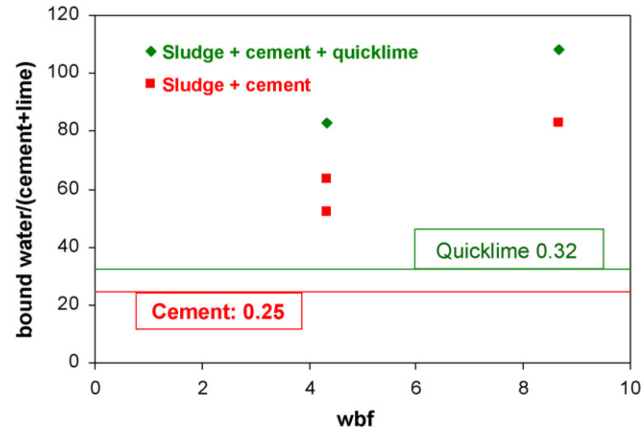

Fig. 5. Chemical water binding (per mass of binder) vs. initial water/binder ratio.

experiments with the dredging sludge with a dry matter content of 35%. The dry matter content of these mixtures was measured after 1, 2 and 4 weeks by drying at 105 °C. The results are presented in Table 4. It appeared that the mass of the hydrated cement (dry matter content of the mix) increased and became stable after approximately 2 weeks with an increase of about 25%, comparable to the value from the literature.

Quicklime reacts with water to form calcium hydroxide ($Ca(OH)_2$). In this reaction for 100 g of quicklime 32 g of water is chemically bound. Subsequently, this calcium hydroxide might react with carbon dioxide (CO_2) to form calcium carbonate ($CaCO_3$) and water. On 100 g of quicklime, almost 75 g of carbon dioxide can be bound. The reactions of cement and quicklime with water/CO_2 are exothermic producing heat that will stimulate the evaporation of water.

The observed amounts of chemically bound water for the experiments with the dredging sludge are also included in Table 4. These numbers suggest that the increase in dry matter content is much larger than the expected 25% for cement and 32% for quicklime alone. For the samples with 15% cement the chemically bound water after 2 weeks was 1.8 kg, which is 39% of the initial mass of cement. After that the amount of chemically bound water increased even further to 51% after 20 weeks. The water/cement ratio for this mixture was 4.3. For the mixtures with cement and quicklime, the amounts of chemically bound water are even higher, even 107% for sample 7/0.5/1. The samples that were regularly turned over had higher percentages of chemically bound water, implying an increased hydration rate. After 4 weeks a slight drop in chemically bound water was noticed. This could be a result of other processes such as the formation of calcium carbonate by which some water is released.

To illustrate the effect of quicklime and water/binding factor (wbf), in Fig. 5 the chemically bound water/binder is set out versus initial water/binder ratio in the sludge. One can readily see that with increasing wbf, more water is chemically bound. This could imply that for the mixes with lower wbf, there is not sufficient water available to achieve the higher chemically bound water ratios achieved with the mixes with higher wbf. Fig. 5 also demonstrates the higher chemically bound water when quicklime is used.

It may be concluded that the presence of the dredging sludge increases the reaction time of cement and quicklime and enhances the formation of chemically bound water. Most likely some minerals in the dredging sludge form new compounds with water, cement, and quicklime, forming more and probably new reaction products that contain a higher amount of chemically bound water than for cement and quicklime alone. Also carbonation might result in an extra mass increase. Mixing the samples improves the dispersion of the binders and consequently provides more optimal conditions for reaction of the cement and quicklime with water/CO_2 and minerals.

5. Contaminant concentrations and immision

5.1. Contaminant concentration

To identify the applicability of the treated material according to the Dutch regulation, the contaminant concentrations and their emissions need to be known. Table 5 shows the contaminant concentrations in the dredging sludge and the standard compositions set by the Building Materials Decree [4]. From this table it can be seen that some constituents exceed SC1 (shaded), but none SC2. This means that the used dredging sludge can be

Table 5
Contaminant concentrations in the dredging sludge and standard compositions according to the Building Materials Decree (all units in mg/kg)

	symbol	dredging sludge	SC1	SC2
Fluoride	F	-	175	-
Chloride	Cl	<10	200	-
Bromide	Br	-	20	-
Sulphate	SO_4	8800	2	-
Arsenic	As	20	29	55
Mercury	Hg	0.28	0.3	10
Cadmium	Cd	1.9	0.8	12
Chromium	Cr	27	100	380
Copper	Cu	42	36	190
Nickel	Ni	24	35	210
Lead	Pb	160	85	530
Zinc	Zn	650	140	720
Molybdenum	Mo	3.3	10	200
Antimony	Sb	4.2	-	-
Selenium	Se	0.03	-	-
Vanadium	V	90	-	-
PAHs		3.75	1	40

Table 6
Emission values (mg/kg) for the original (E_i) and treated samples

	symbol	E_i	$E_{0/0/1}$	$E_{7/½/1}$	$E_{14/1/0}$	$E_{15/0/0}$	E_{max}[a]
Acidity	pH		6.5	10.28	11.6	10.2	
Fluoride	F	3.7	1.9	1.8	2.2	3.6	3.0
Chloride	Cl	-	570	520	90	40	51
Bromide	Br	0.5	2.1	0.5	1.3	1.5	2.6
Sulphate	SO_4	2200	1200	2400	5500	7100	354
Arsenic	As	0.17	0.12	0.14	0.20	0.075	0.7
Mercury	Hg	0.0003	0.0003	0.0003	0.0003	0.0003	0.016
Cadmium	Cd	0.001	0.001	0.001	0.001	0.001	0.021
Chromium	Cr	0.02	0.02	0.02	0.02	0.02	0.09
Copper	Cu	0.02	0.90	0.38	0.37	0.02	0.25
Nickel	Ni	0.05	2.50	1.80	0.45	0.05	0.63
Lead	Pb	0.05	0.05	0.06	0.05	0.05	0.8
Zinc	Zn	0.21	0.025	0.035	0.10	2.50	2
Molybdenum	Mo	80	950	1000	1100	330	0.45
Antimony	Sb	5	200	200	300	200	0.06
Selenium	Se	10	500	500	500	500	0.09
Vanadium	V	70	900	3000	2900	170	1.2

[a] E_{max}, maximum permissible emission (mg/kg).

classified as Category 1, Category 2 or as Not Applicable (see Section 1 and Fig. 1). The final classification depends on the emission, which is discussed in the following section.

5.2. Leaching behavior

Leaching tests are performed to investigate the emission of contaminants from the dredging sludge before and after treatment. The emission in mg/kg for the different constituents was calculated from the measured concentrations in the effluent [14]. Table 6 shows the results of the leaching tests. E_i is the emission value of the original, untreated dredging sludge, for the others the same codes are used as before. In the last column the maximum permissible emission according to the Building Materials Decree [4] is given. With shades the values exceeding this maximum value are marked. For the untreated sludge the emission of fluoride, sulphate, and four exotics (molybdenum, antimony, selenium and vanadium) are exceeded. Unfortunately, the measurement for chloride was not successful. The emission values of the ripened (lower dm) dredging sludge are relatively low, but during ripening organic matter is oxidized and the pH is altered, enabling the release of some compounds. A glance at the emission of the sample 0/0/1 without binders after ripening (Table 6), indeed, reveals that the emission of some elements has increased significantly. Besides the values of sulphate and the exotics, also the values of copper and nickel exceed the maximum permissible emission. On the other hand, the value for fluoride has dropped below E_{max}. The values for all other constituents are also below E_{max}.

Ripening increases the emission (compared to fresh dredging sludge), but ripening cannot be avoided as it always takes place in order to reduce the water content (to increase the dm). But comparing untreated (reference, i.e. ripened without binder) and treated sludge (with binders), one can see substantial changes in pH and in leaching (for the relevant contaminants). By mixing cement and quicklime the following changes can be observed in the leached concentrations. The values of chloride, copper and nickel decrease with increasing amount of cement. The values for the samples with 15% cement even drop below the maximum emission level. However, there are also constituents, like fluoride and zinc, for which the emission increases when cement is added. For the 15% cement addition the emission of these constituents even exceeds the maximum value. For both constituents, the combination with quicklime shows a smaller increase, then the emission remains below E_{max}.

To get an impression of the applicability of the treated dredging sludge, the maximum height (h) to which the dredging sludge may be applied is calculated. The computation is based on the concentration that can be expected from this height at the bottom of the piled material (derived from the emission values), and the maximum permissible concentration of water that imbibes into soil or surface water. This is shown in Table 7. For the constituents without any mark the application of dredging sludge has no limitations, i.e. an application height of 10 m or more. The crosses indicate that the emission of these constituents is so high that the permissible application height is less than the

Table 7
Maximal application height (m) as Category 1 building material according to the Building Materials Decree [2]

Constituent	Symbol	$h_{0/0/1}$	$h_{7/0.5/1}$	$h_{14/1/0}$	$h_{15/0/0}$
Fluoride	F				
Chloride	Cl	2.0			
Bromide	Br				
Sulphate	SO_4	x	x	x	x
Arsenic	As				
Mercury	Hg				
Cadmium	Cd				
Chromium	Cr				
Copper	Cu	0.5	3.0	3.0	
Nickel	Ni	x	0.2		
Lead	Pb				
Zinc	Zn				3.0
Molybdenum	Mo	x	x	x	x
Antimony	Sb	x	x	x	x
Selenium	Se	x	x	x	x
Vanadium	V	x	x	x	x

Table 8
Actual and maximal concentrations for the exotic constituents (in mg/kg) according to the Building Materials decree

Eluate	Symbol	c_0	c_{max}
Molybdenium	Mo	3.3	101.5
Antimony	Sb	4.2	9
Selenium	Se	0.03	50.35
Vanadium	V	90	146

minimum height of 0.2 m, which makes the sludge unsuitable for application.

The Building Materials Decree has been adapted (relaxed) at several points in the past years. The limitations for fluoride, bromide, and sulphate have been canceled. Fluoride and bromide were not a problem, but the exemption for sulphate takes away one of the constraints for the applicability (Table 7).

For the four exotics (molybdenum, antimony, selenium and vanadium) a new regulation has been formulated. When the concentration of these constituents is below a certain maximum concentration (c_{max}) they do not have to be tested on their emission. In Table 8 this maximum concentration is given as well as the concentration of these constituents in the dredging sludge (c_0). The concentrations of all exotics are below c_{max}. The last two columns of Table 7 indicate that the treated dredging sludge can be considered a Category 1 building material with a maximum application height of 3 m, as the copper and zinc concentrations are slightly exceeded.

6. Conclusions

The objectives of this research were to investigate the effect of binders on the ripening process and immobilization of dredging sludge. An important measure for the applicability of treated dredging sludge is the consistency. Below dry matter contents of 50–55% the dredging sludge is too wet to be used as a building material. During the experiments the dry matter content was measured in time by the mass decrease (loss of water by evaporation) and by drying at 105 °C. The samples in which binders were used showed a faster increase in dry matter content than the samples containing no binders. Also the samples that were turned over regularly, increased more rapidly in dry matter content.

The apparent dry matter contents calculated from mass loss were consistently lower than the actual dry matter content determined by drying at 105 °C. This means that the water that reacts with the cement and quicklime is chemically bound and is not released at 105 °C. Cement alone reacts with water with a mass ratio of 25 g water on 100 g cement (water retained at 105 °C). In a mixture with dredging sludge the cement and quicklime retained much more water, from about 50 g to over a 100 g of retained water to 100 g of added cement and quicklime. This chemical binding of water, in which most likely minerals from the sludge are also involved, enhances the increase in dry matter content, and accelerates the ripening process such that the material has reached the required consistency more rapidly. By adding 7% cement and 0.5% quicklime the ripening process is accelerated by a factor of 3. Larger amounts of binder do not accelerate the ripening process proportionally; also less water is chemically bound in such case.

Another important aspect for the applicability of treated dredging sludge is the contaminant concentration and their emission. In this study dredging sludge with the highest level of contamination, Class 4, was used. The contaminant concentrations were low enough to prevent the dredging sludge to be classified as Not Applicable. The emission of sulphate, copper, nickel and four exotic elements (molybdenum, antimony, selenium, and vanadium) exceeded limits for unrestricted application as Category 1 building material. However, recently the regulations have been relaxed for several compounds. For fluoride, bromide and sulphate the emission, limits have been canceled. The exotics have to be below a certain maximum concentration. This was the case for the used dredging sludge such that it could be classified as a Category 1 building material, with a maximum height of 3 m (due to the emission of zinc and copper). For treatment of other dredging sludge it is important to establish the effect of cement and quicklime on the leaching. The addition of cement has a negative effect on sulphate, fluoride, and zinc. On the other hand, cement reduces the emission of chloride, copper, and nickel. Although quicklime increased the emission of some constituents and reduced it for others, it does not negatively affect the qualification of the end product.

The optimal amount of cement and quicklime to enhance ripening and immobilization of the dredging sludge depends, among other things, on the cocktail of contaminants in the treated dredging sludge. When large concentrations of chloride and nickel are present in the sludge, it is recommended to add 15% of binder. In other cases 7% cement and 0.5% quicklime is sufficient to facilitate the ripening process and obtain a Category 1 building material with maximum height of 3 m. Anyway, a Category 2 building material seems feasible under almost all conditions.

This research showed that the use of binders accelerates the ripening process and affects the immobilization of contaminants in such a way that it is an attractive method for treating dredging sludge. Based on this research, a large-scale experiment is planned to treat urban dredging sludge, of the highest contamination Class 4, with cement and quicklime and possibly also some gypsum [17], in order to render the product applicable for civil works (and prevent sludge from being disposed).

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