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SMOCS (Sustainable Management of Contaminated Sediments in Baltic Sea Region)
Analytical tests

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Index

1. INTRODUCTION

WP1 – administrative WP. Several meetings have been attended by a representative from LUT or by a proxy.

In the project, there is an approach that will utilize different contacts widely. For this, a list of contacts and possible target groups has been collected. This list includes administrative bodies as well as stakeholders and problem owners. This list has been submitted to WP2 leader. WP2 as being the WP for communications, has been attended to several meetings – some in the phone and some as "regular" meetings.

The basic knowledge has been gathered of the subjects relevant to the project. Common sediment properties and contamination has been investigated in Finnish region. This has been collected to WP4 leader. Data has been collected about Finnish legislation concerning waste materials and contaminated sediments, which has been sent to WP4 leader, who will combine these data to a file explaining the situation overall Baltic Sea Region.

Regarding stabilization and other methods for handling of sediments, these methods have been reviewed for understanding the procedure. Binders that can be used for stabilization have been investigated – in the sense what is available in Finland and in Estonia. This has been sent to WP5 leader that will utilize this data as appropriate.

Regarding WP6, some actions are listed either in WP4 or WP5. For WP4 has been included the analysis of the sediments – their physical and chemical properties. This has been investigated for samples from Kokkola and from Kymijoki. The samples have been analyzed for their organic matter content and for inorganic compounds. Inorganic cations have been analyzed with ICP-OES (inductively coupled plasma optical emission spectrometer) and anionic content with ion chromatography. Different binder materials have been analyzed for their chemical composition with ICP. This has been seen as a crucial point in understanding the mechanisms of their behavior.

Studies concerning chemical properties during stabilization are included in WP5 – state of the art technologies. Studies have been conducted with samples from Kokkola using several binder materials and their combinations. Physical properties have been analyzed by Ramboll Finland via sub-contracting (and similar test pieces will be done in LUT in order to find chemical leaching properties).

For leaching testing of stabilized material different methods have been investigated. A common method is to analyze it by "2-stage batch test" or by an up-flow percolation test. However, in several occasions these may not give the real result of the behavior. A more novel method is the diffusion testing based on Dutch pre-standard NVN 7347. This defines the leaching as the cumulative leachability of the stabilized piece covered with Teflon tape on other sides but the top which is covered with glass beads. This is then immersed in deionized water for 4, 16 and 64 days. The water is thus changed three times and analyzed separately. Most probably this method will increase its popularity, but at the moment the legality is still unsure.

2. ANALYZED SEDIMENTS

Samples have been investigated from

- Port of Kokkola (2 parallel samples)
- River Kymijoki (initial concentrations from both surface and bottom). Samples were aggregate samples from three points. Sampling was taken by a diver, Figures 2.1 and 2.2.
- Port of Gdynia
- Port of Gävle

Initial properties (moisture and residue) and total metal content from sediments were investigated as the total metal content in sediment with ICP-OES. Moisture and total residue were analyzed as standardized methods. The procedures follow standards SFS-EN 14346 for water content and total residue, SFS-EN 13346 for aqua regia extraction of sediment and SFS-EN ISO 11885 for analysis with ICP. Mercury content was analysed with CV-AAS (cold vapour atomic absorption spectrometer) according to standards. Analyses from Port of Gdynia are done in Maritime Institute in Gdansk.

Figure 2.1 Surface sample from river Kymijoki

Figure 2.2 Bottom sample from river Kymijoki

2.1 ICP results of sediments

The sediments were initially studied for metal contaminants (and content) with ICP-OES (Inductively Coupled Plasma Optical Emission Spectroscopy). Contaminants from Port of Gdynia was obtained via Maritime Institute in Gdánsk. Results are shown in Table 2.1.

Table 2.1 Initial contaminants (ND = non-determinable, BD = below detection limit). Threshold limit for total concentrations exceeded → bold, lower guideline limit exceeded → double borders, upper guideline limit exceeded → gray background.

mg/kg(dw.)	Kymijoki surface	Kymijoki bottom	Kokkola 1	Kokkola 2	Gdynia
Al	1967.6	2834.8	972	1176	
As	BD	BD	22.6	24.6	
Ca	266.5	276.1	224.3	271.7	
Cd	ND	ND	ND	ND	1.2
Co	12.8	16.5	14	14.7	11.4
Cr	6.1	4.7	4.3	5	23.6
Cu	35.7	34.7	44.1	44	276.3
Fe	2689.6	3364.3	4202	4679.9	
K	321.2	562.8	151.4	247.8	
Mg	396.3	568	254.9	270.3	
Mn	BD	69.2	31.5	20.4	
Na	1131	608	803	664.1	
Ni	23.2	26.3	24.8	24.9	12.7
Pb	23.2	15.8	21.4	24.3	187.7
Zn	58.9	61.6	512.6	560.2	498.3
Hg	4.6	6.7	0.2	BD	0.2

Finnish guideline values for total concentrations are shown in Table 2.2.

Table 2.2 Finnish guideline values for total concentrations

METAL	TRESHOLD	LOWER LIMIT	UPPER LIMIT
		mg/kg	mg/kg
Arsenic (**As**)	5	50	100
Cadmium (**Cd**)	1	10	20
Chromium (**Cr**)	100	200	300
Copper (**Cu**)	100	150	200
Lead (**Pb**)	60	200	750
Mercury (**Hg**)	0.5	2	5
Nikel (**Ni**)	50	100	150
Zinc (**Zn**)	200	250	400

2.2 Moistures and residues

Moistures and total residues (Loss On Ignition), Table 2.3, were determined for all sediment matrices based on standard methods.

Table 2.3 Index properties moisture and total residue of sediments

	[%]	[mg/g]
	Moisture	Total fixed residue
Kokkola	36.4	980
Kymi bottom	78.9	830
Kymi surface	84.3	812
Gdynia	64.6	925
Gävle	77.1	859

3. Stabilization binders

In the experiments. binder material selection is based on the following options:

Cement (Yse) is a common commercial binder that represents regular quality. A similar product is available in all countries around the Baltic Sea. Here the manufacturer is Finnsementti.

Oil shale ash (PKT) is fly ash originating from burning of oil shale in Eesti Energia power plant in Narva. Estonia. These ashes vary a lot based on power plant and the technique of burning.

Fly ash (LT) originates from Alholmens Kraft mixed burning facility (wood. peat. coal) in Pietarsaari. Finland. Fly ash can have a lot of different qualities based on. e.g.. technique of combustion and raw material. The current ash has been previously found highly reactive and suitable for binder in sediment stabilization. Testing of that ash will provide a good estimate of the performance in stabilization work.

Gypsum (DI) originates from Yara Finland manufacturing plant in Siilinjärvi. Finland. Gypsum exists in several different forms, but in this case as a binder dihydrate gypsum is investigated. Gypsum has been stored outdoors in a pile. In previous studies it has been found to have a positive effect on the strength of the stabilized material.

Slag (KJ. K400) is a commercial binder that has been previously under the status of a by-product. Slag is being manufactured by granulating and grinding slag from production of raw iron.

3.1 Analyses of binder materials

Moistures and residues were analyzed for used binder materials, Table 3.1. Binders were analyzed for their active calcium content based on the standard SFS 5188, Table 3.2. Acidity of gypsum prevented the analysis. Binders have the following concentrations of metals based on ICP-OES analysis and *aqua regia* digestion, Table 3.3.

Table 3.1 Index properties moisture and total residue for used binder materials

		[%]	[mg/g]
Binder	Origin	moisture	residue
Oil shale ash	Eesti Energia	0.22	995
Fly ash	Gdynia	0.17	945
dihydrate gypsum	Yara Siilinjärvi	23.69	953
GTC	Commercial	4.01	945
K400	Commercial	0.18	995
Yse (cement)	Commercial	0.55	996
Rapid cement (pika)	Commercial	8.19	995
Fly ash (LT)	Alholmens Kraft	0.31	983

Table 3.2 Active calcium content of binder materials based on sugar-method

	Act Ca %
Oil shale ash	6.5
Rapid cement (pika)	10
K400	0.8
YSe	17.9
dihydrate gypsum	---
Fly ash (LT)	2.8
GTC	10.8

Table 3.3 Metal concentrations of binder materials (ND = non-determinable, BD = below detection limit). Threshold limit for total concentrations exceeded → bold, lower guideline limit exceeded → double borders, upper guideline limit exceeded → gray background.

	Fly ash (LT)	gypsum	GTC	K400	Oil shale ash
Al	6763.8	25.0	146.6	348.1	405.0
As	18.9	BD	BD	BD	BD
Ca	6634.7	771.1	2581.3	1608.4	2229.5
Cd	ND	ND	ND	ND	ND
Co	25.0	9.9	8.1	6.1	7.6
Cr	15.6	ND	ND	ND	ND
Cu	161.2	21.0	20.0	18.5	22.0
Fe	8723.3	46.0	132.6	131.2	486.7
K	1798.7	248.9	121.5	201.5	685.5
Mg	1464.2	82.3	64.8	311.9	225.9
Mn	135.6	157.6	70.2	44.9	102.5
Na	4873.8	3093.7	1088.9	2125.6	2243.5
Ni	31.5	21.2	19.4	17.5	20.9
Pb	41.2	16.7	13.6	15.5	15.7
Zn	289.8	13.5	11.9	10.8	13.6

3.2 Settings and binder amounts

Samples from Port of Gdynia were prepared by Maritime Institute in Gdansk and analyzed in LUT, Table 3.4.

Table 3.4 Tested binder materials on sediment sample from Port of Gdynia.

Sample #	binder materials [kg/m3]					
Sediment (GDA)	cement	slag	oil shale ash	fly ash (LT)	fly ash (Gdynia)	gypsum
8	75	75				
12	75		200			
20	75			200		
22	75				200	
25	75	75		75		75
32	75	75		75		
33	75	75	75			

Kokkola (KLA) and Kymijoki (KY) sediments were analyzed with the following setup. These samples were analyzed using diffusion leaching test. Binder mixtures are selected based on compression testing in Ramboll Finland.

Table 3.5 Samples for diffusion testing with Port of Kokkola and Kymijoki matrices.

	Binder	Volume
KLA BL	-	0
KLA 1	*Yse*	30
KLA 2	*Yse*	100
KLA 3	*LT*	200
KLA 4	*Yse LT*	30 200
KLA 5	*YSe PKT*	30 100
KLA 6	*Yse PKT*	30 200
KLA 7	*Yse PKT DI*	30 50 50
KY BL	-	0
KY 1	*Yse*	200
KY 2	*Yse*	300
KY 3	*Yse PKT*	150 200
KY 4	*Yse PKT*	200 100
KY 5	*Yse LT*	150 200
KY 6	*Yse LT*	200 100
KY 7	*Yse DI*	200 100

Batch test experiments were done on Kymijoki and Kokkola samples following experimental designs as shown in Tables 3.6-3.9. The testing consists of a set of samples with fly ash and a set of samples with oil shale ash for both sediment matrices.

Table 3.6 Binder ratios for Kokkola sediment. The unit for binders is kg/m^3.

#Mixture	fly ash	gypsum	slag	cement =constant
1	100	100	100	50
2	0	100	100	50
3	100	0	100	50
4	0	0	100	50
5	100	100	0	50
6	0	100	0	50
7	100	0	0	50
8	0	0	0	50
9	50	50	50	50
10	50	50	50	50
11	50	50	50	50

Table 3.7 Binder ratios for Kokkola sediment. The unit for binders is kg/m^3. * Corresponding mixtures done in design ”Table 3.6” → samples are not done

#Mixture	oil shale ash	gypsum	slag	cement =constant
12	100	100	100	50
13*	0	100	100	50
14	100	0	100	50
15*	0	0	100	50
16	100	100	0	50
17*	0	100	0	50
18	100	0	0	50
19*	0	0	0	50
20	50	50	50	50
21	50	50	50	50
22	50	50	50	50

Table 3.8 Binder ratios for Kymijoki sediment. The unit for binders is kg/m^3.

#Mixture	fly ash	gypsum	slag	cement =constant
23	100	100	100	100
24	0	100	100	100
25	100	0	100	100
26	0	0	100	100
27	100	100	0	100
28	0	100	0	100
29	100	0	0	100
30	0	0	0	100
31	50	50	50	100
32	50	50	50	100
33	50	50	50	100

Table 3.9 Binder ratios for Kymijoki sediment. The unit for binders is kg/m^3. * Corresponding mixtures done in design "Table I_c" → samples are not done

#Mixture	oil shale ash	gypsum	slag	cement =constant
34	100	100	100	100
35*	0	100	100	100
36	100	0	100	100
37*	0	0	100	100
38	100	100	0	100
39*	0	100	0	100
40	100	0	0	100
41*	0	0	0	100
42	50	50	50	100
43	50	50	50	100
44	50	50	50	100

Experiments were done with sediment matrix from Port of Gävle following an experimental design and an approximate binder composition found feasible in the field test, Table 3.10. It was also considered if oil shale ash was used, Table 3.11.

Table 3.10 Binder ratios for Gävle sediment. The unit for binders is kg/m^3.

#Mixture	Fly ash (Sweden)	gypsum	Merit (slag)	cement =constant
1	50	25	25	50
2	50	25	0	50
3	0	25	25	50
4	0	25	0	50
5	50	0	25	50
6	50	0	0	50
7	0	0	25	50
8	0	0	0	50
9	25	12.5	12.5	50

Table 3.11 Binder ratios for Gävle sediment. The unit for binders is kg/m^3.

#Mixture	Oil shale ash	Merit (slag)	cement =constant
1	50	25	50
2	50	0	50
3	0	25	50
4	0	0	50
5	25	12,5	50

3.3 Stabilization procedure

Stabilization tests are done for the effect of different types and quantities of binders on the properties and on the performance of the stabilized base material. The tests can include testing of unconfined (1-axial) compression strength (UCS) after a 28 days hardening / curing period and leaching testing with diffusion testing or batch testing according to standardized procedures.

Sediment material will always segregate and water will rise above solid matter and the sediment must be well homogenized before a stabilization amount is extracted, Figure 3.1.

Figure 3.1 Homogenizing settled sediment material

A representative sample of sediment will be mixed with designed amount of binder materials. The quantity of the binder will be determined with a certain amount of dry binder (kg) in relation to the volume (m^3) of wet soil/base material, Figure 3.2.

Figure 3.2 Sediment is mixed with dry binder materials

The mixing is done with a common household mixer with a constant workload of two minutes/batch. During mixing, the material is removed from the walls of the mixing bowl, Figure 3.3.

Figure 3.3 Mixer

After mixing the material is placed to test piece tubes for the hardening period. Care should be taken not to have large holes in the material. The material can be slightly compressed to the tube using, e.g., a wooden tool. Figure 3.4 shows the process of material packing.

Figure 3.4 Making of test pieces

After the test piece tubes have been made the tubes will be put into plastic bags or sealed to avoid drying and stored for a specific period and at specific conditions before start of testing, Figure 3.5. Normally, for the first two days the test pieces will be stored at rooms temperature (around +20°C) packed in insulation boxes in order to keep them in a constant climatic condition. After this the storage temperature will often be around +8°C for the rest of the hardening period. Hardening can be done in 35 ºC or in room temperature.

Figure 3.5 Acrylic test tube with stabilized sediment in it

After required hardening period, the stabilized pieces are pushed out from the tubes. The pieces are judged based on their conditions (homogeneity, cracks, holes, etc.). Stabilized pieces are shown in Figure 3.6.

Figure 3.6 Stabilized samples

The mixing bowl, tubes and other equipment for the mixing will be chosen with respect to the material specific requirement that have been agreed on for the stabilization test program. For instance in case of chemical testing for heavy metals of the stabilized samples all possible contamination will be avoided with help of non-metallic equipment.

3.4 Tests for leaching

3.4.1 Modified diffusion test

The modified diffusion test is based on the Dutch draft standard NVN 7347 from 1999. Originally the standard is intended to use for determination of the leaching of inorganic components from compacted granular materials. For example Technical Research Centre of Finland has applied this standard for studying the leaching characteristics of solidified/stabilized clayey and slurry materials. According to the standard test piece is immersed in water adjusted to pH 4 (with nitric acid) for 64 days and the water is replaced 8 times during that period (after 6 h, 1 d, 2.25 d, 4 d, 9 d, 16 d, 36 d and 64 d). The results of this leaching test are reported as the cumulative mass of dissolved compounds versus the top surface area of the test piece (in mg/m^2) as a function of time. The test has also been applied to determine only 4 d, 16 d and 64 d cumulative emissions as a function of time.

The experimental procedure is as follows: After stabilization the test piece will be taken out from the plastic cylinder and covered all over with Teflon tape except the top surface area. The top surface area will be covered with 1 cm thick layer of Ø 2 mm glass beads, Figure 3.7, and the sample will be immersed in deionized water adjusted to pH 4 with nitric acid, Figure 3.8. The volume, pH, electrical conductivity, Redox-potential and the concentrations of components in question will be determined from each water sample.

Figure 3.7 A test piece for modified diffusion test

Figure 3.8 Modified diffusion testing

3.4.2 Batch test

The sample is tested according to standard ”*SFS-EN 12457-3. Characterisation of waste. Leaching. Compliance test for leaching of granular waste materials and sludges. Part 3: Two stage batch test at a liquid to solid ratio of 2 l/kg and 8 l/kg for materials with high solid content and with particle size below 4 mm (without or with size reduction*”.

The sample material which has a particle size below 4 mm (originally or with size reduction) is brought into contact with water under specified conditions. The test is serial batch leaching test consisting of two steps. The test provides information on leaching of inorganic constituents from granular wastes and sludges in a liquid to solid ratio of 2 l/kg dry matter in a first step (6 h) and subsequently of 8 l/kg dry matter in a second step (18 h), Figure 3.9. The standard is based on the assumption that equilibrium is achieved between the liquid and solid phases during the test period. The solid residue is separated by filtration and the properties of eluates are measured (electrical conductivity, pH, Redox-potential and the concentrations of components in question). The test does not take into account the particular characteristics of non-polar organic constituents nor the consequences of microbiological processes in organic degradable wastes. The procedure is only applicable to waste material and sludges having a high solid content: the dry matter content ratio shall be at least higher than 33%. The results will be expressed as mg of the components released cumulatively per kg of test material (dry matter) in the L/S ratio 10.

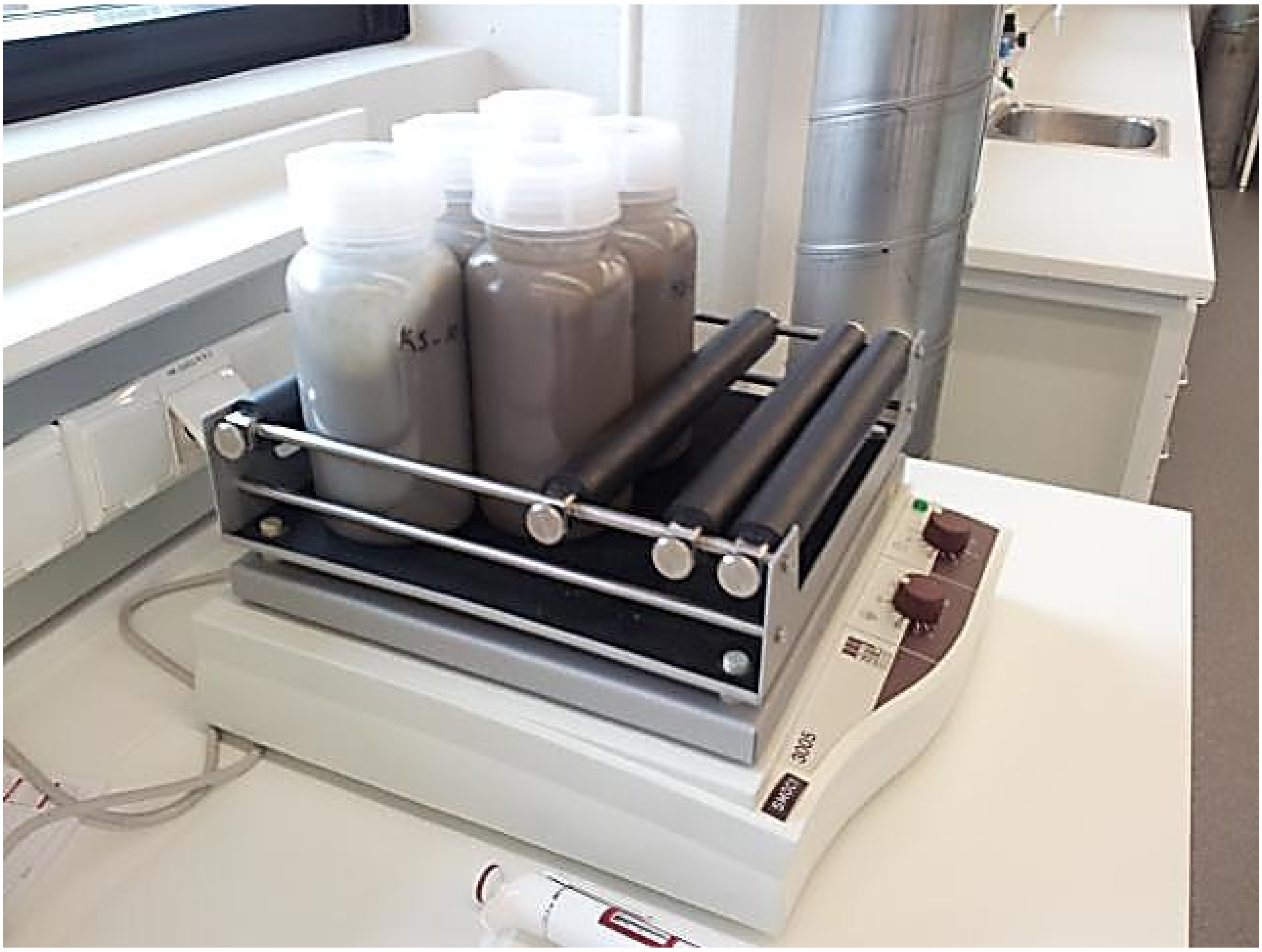

Figure 3.9 Batch testing L/S 8 ratio on stabilized sediment samples on-going in an orbital shaker.

Leachates were analyzed with ion chromatograph, Figure 3.10, for anions and with ICP-OES, Figure 3.11, for cations.

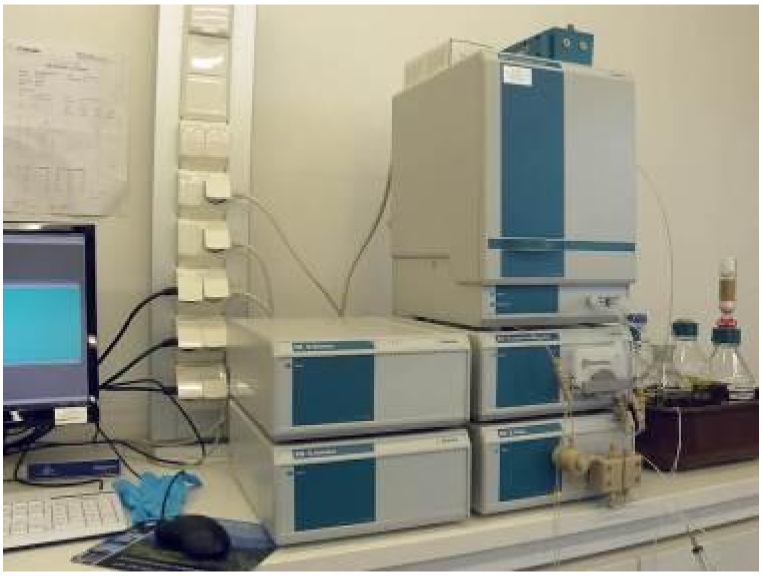

Figure 3.10 Ion chromatograph

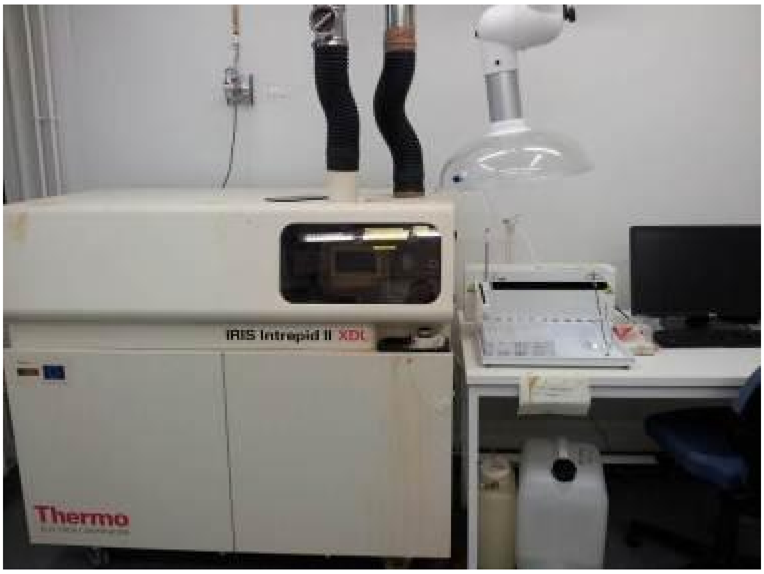

Figure 3.11 Inductively coupled plasma optical emission spectrometer (ICP-OES)

4. Results

4.1 Comparison of the methods

The two different leaching methods were compared. This has not been done earlier and the interest was raised to find out whether there is a correlation between those. It is assumed that the modified diffusion test gives a result of physical stabilization as the material is not broken and only diffusion takes place in the sediment.

Batch test on the other hand requires the material particle size distribution to be modified in less than 4 mm fraction. This way this is assumed to give more the chemical stabilization result than physical. More so results of those methods are given in different units; mg/m2 for diffusion test and mg/kg for batch test. For calcium, no correlation was detected between the methods, Figure 4.1.

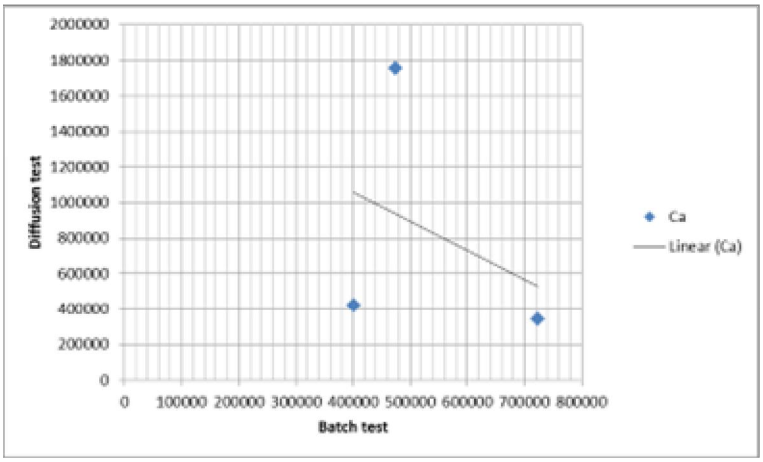

Figure 4.1 No correlation was found between the two methods and calcium leaching

Only with potassium a correlation could be found, Figure 4.2. Otherwise it can be concluded that the methods indicate totally different situations.

During diffusion testing, the pH value changes due to acidic or base group that leach from the sample. Cement reactions form calcium hydroxide as a by-product that are water soluble and provide base OH^- -groups. Due to the fact that in Kymijoki samples, more cement was used, the pH value is high throughout the testing – average around 11. In Port of Kokkola samples, most of the hydroxyl groups appear to release during the first four days. However, long-term release can still be seen in 64 days samples. pH values are shown in Figure 4.3.

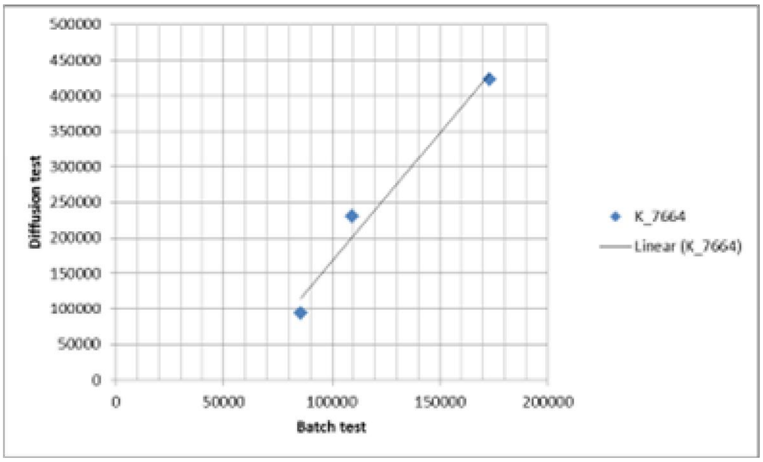

Figure 4.2 Correlation between the two methods

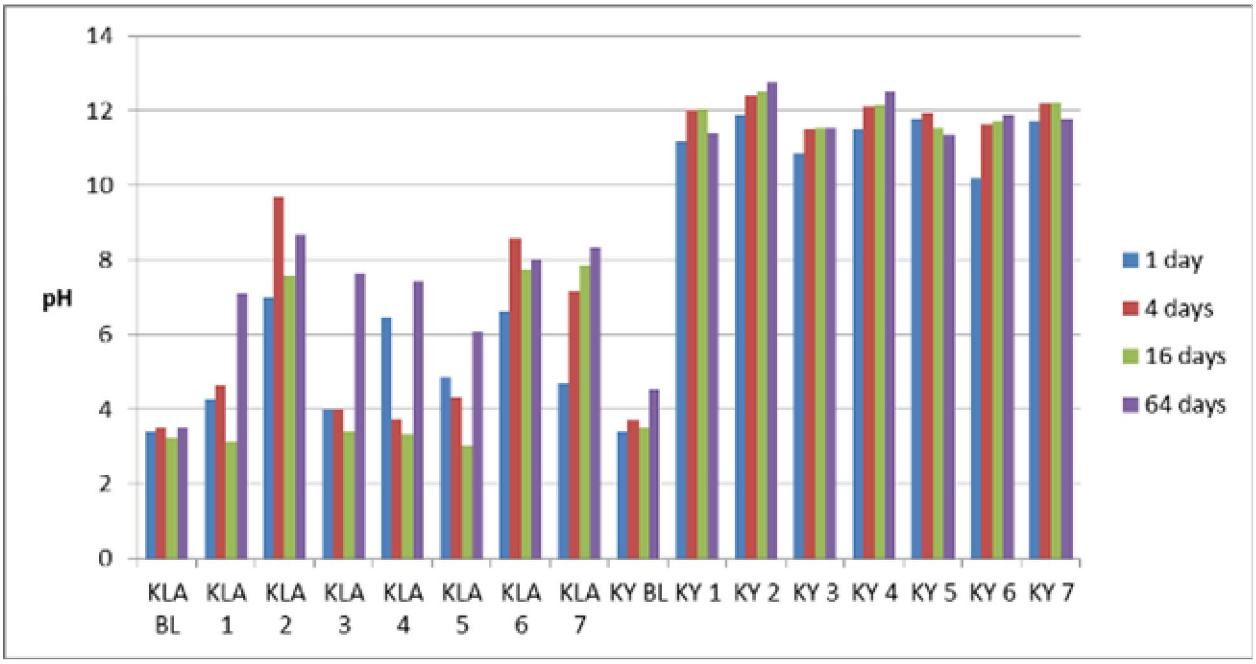

Figure 4.3 pH values of diffusion solutions during testing. Initial pH was set at 4 for each solution with nitric acid

4.2 Port of Kokkola

Stabilization was studied with 2-stage batch testing of stabilized samples. Applied binders and amount are shown in Table 4.1.

Table 4.1 Compositions of experiments following designs of experiments for Kokkola sediment.

		kg/m^3				
		Fly ash	Oil shale ash	gypsum	slag	cement
B	1	Untreated sample				
A	1	100	0	100	100	50
A	2	0	0	100	100	50
A	3	100	0	0	100	50
A	4	0	0	0	100	50
A	5	100	0	100	0	50
A	6	0	0	100	0	50
A	7	100	0	0	0	50
A	8	0	0	0	0	50
A	9	50	0	50	50	50
A	10	50	0	50	50	50
A	11	50	0	50	50	50
A	12	0	100	100	100	50
A	14	0	100	0	100	50
A	16	0	100	100	0	50
A	18	0	100	0	0	50
A	20	0	50	50	50	50
A	21	0	50	50	50	50
A	22	0	50	50	50	50

Measured water content was rather constant in all stabilized samples, close to the average 26 %. These are shown in Figure 4.4. pH values tend to show higher values in L/S 8 solution with few exceptions, Figure 4.5. The addition of gypsum seems to lower the pH value, most specifically in L/S 2 batch.

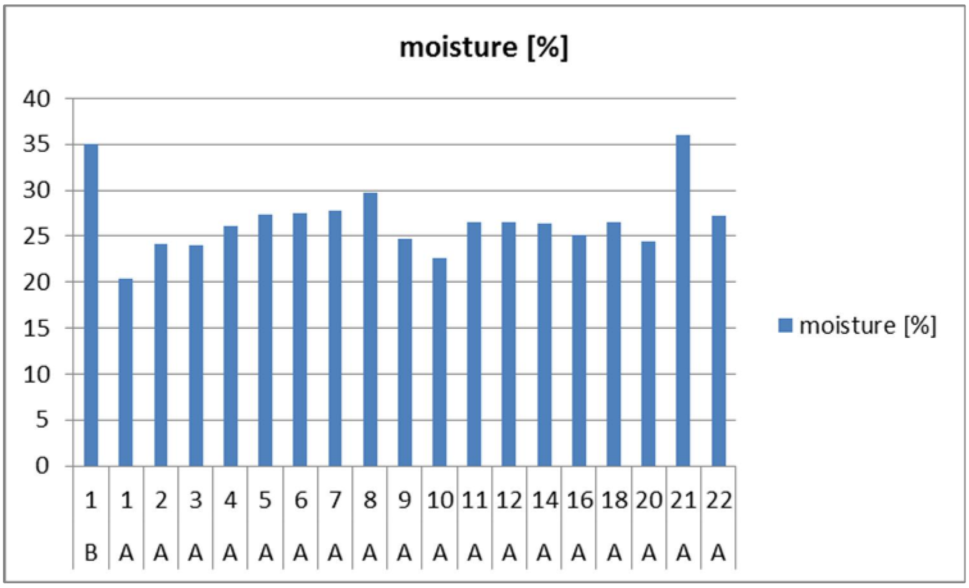

Figure 4.4 Measured water contents of samples prior to batch testing. Sample coding according to Table 4.1.

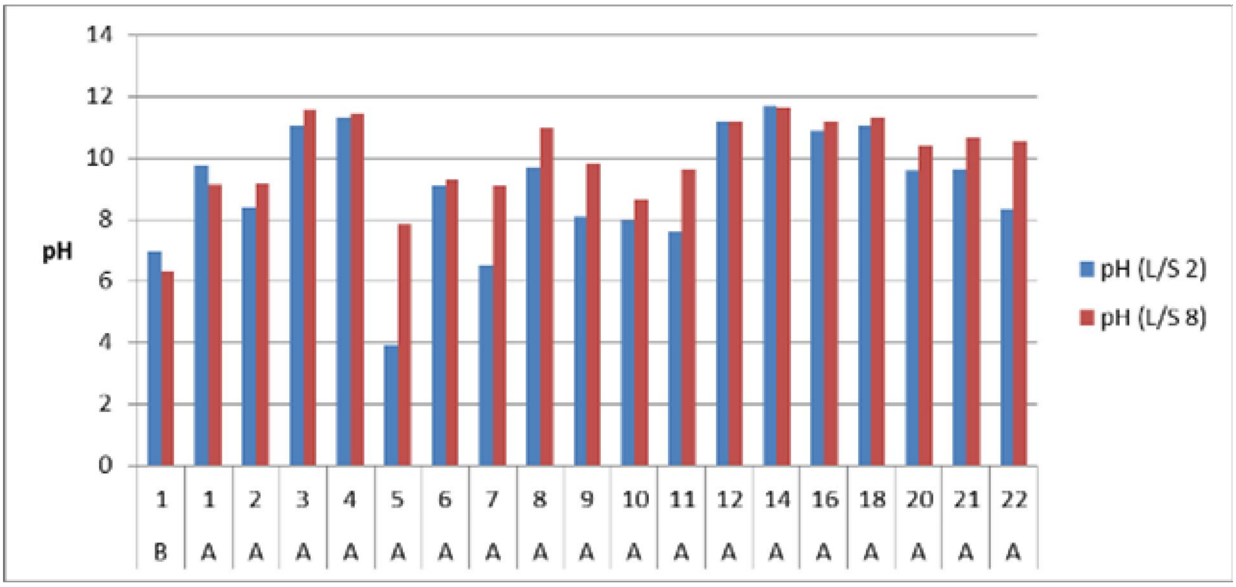

Figure 4.5 Measured pH values from batch testing solutions. Sample coding according to Table 4.1.

In the sediment from Port of Kokkola concentration of zinc was found the main problem. The original leaching of zinc was measured 42.0 mg/kg. This clearly exceeds the limit for inert waste but stays below the limit for common waste (50 mg/kg). Studies show that this could easily be stabilized into non-mobile form as none of the stabilized samples exceed the limit for inert waste solubility, Figure 4.6.

Unsuccessful selection of binder materials could result in more leaching of some elements. This was found with copper, Figure 4.7. Original unstabilized sample has a solubility less than the limit for inert waste. However, all stabilized samples result in concentrations exceeding the limit. The concentrations still stay low and clearly fall below the limit for common waste (50 mg/kg).

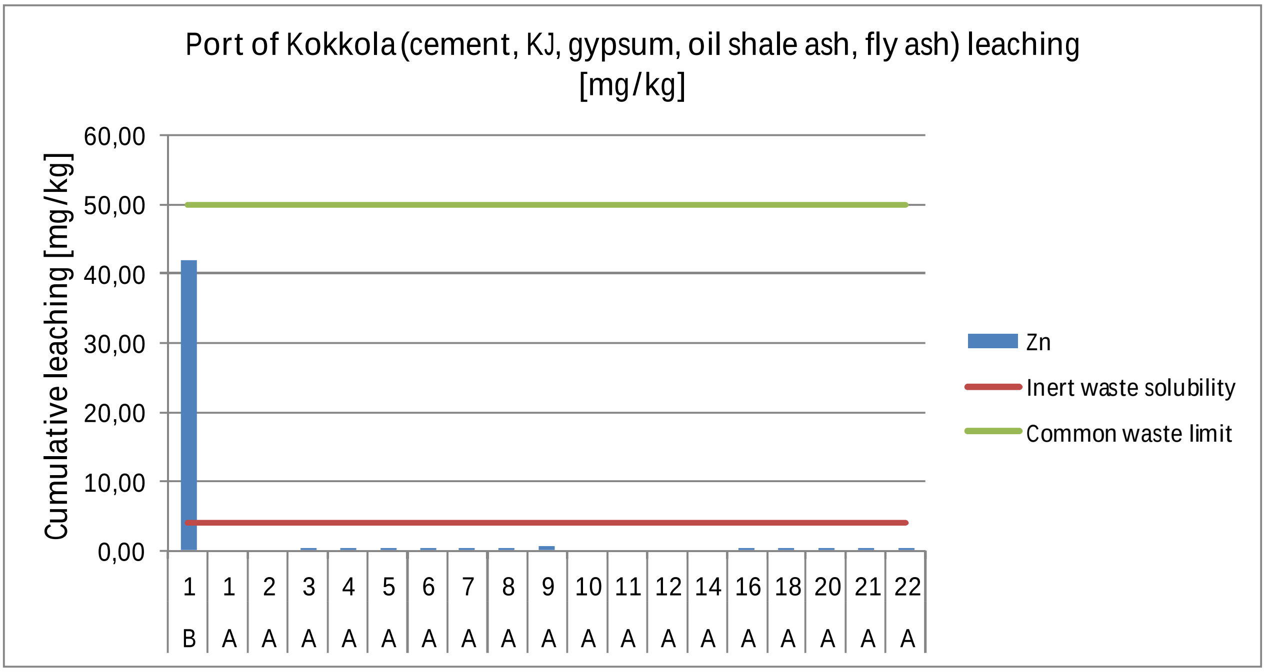

Figure 4.6 Solubility of zinc (original and stabilized samples). Sediment matrix is from port of Kokkola. Sample coding according to Table 4.1.

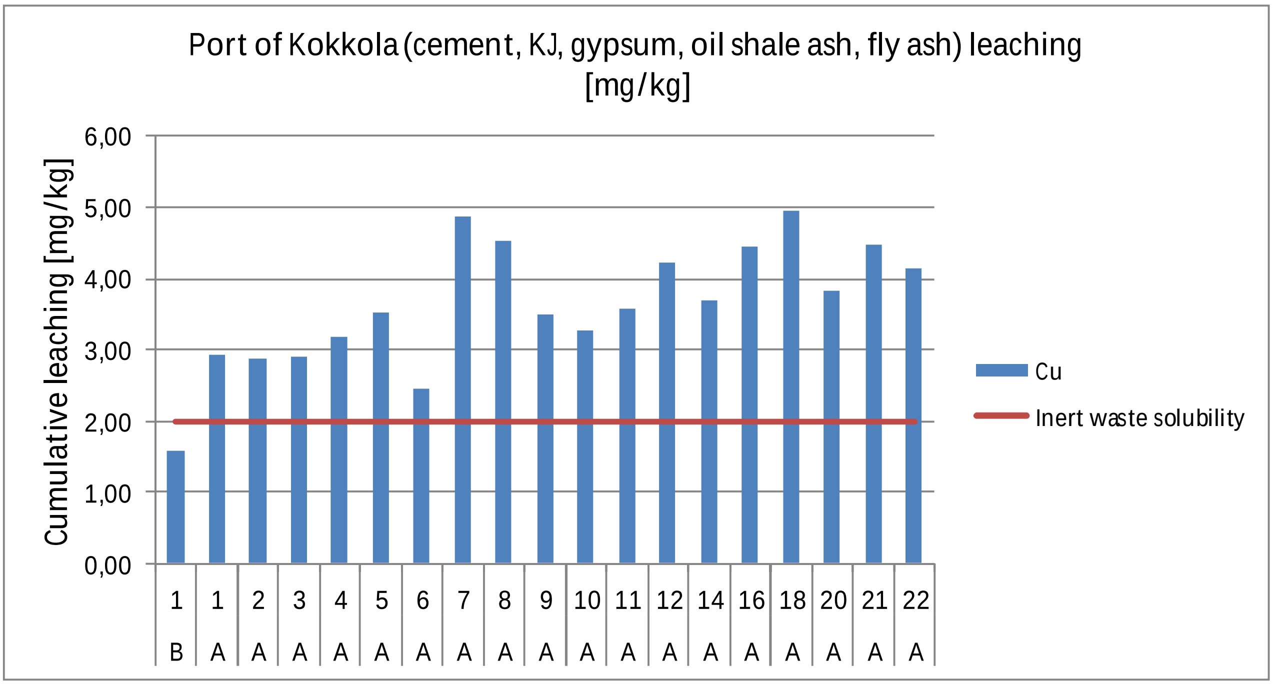

Figure 4.7 Solubility of copper (original and stabilized samples). Sediment matrix is from port of Kokkola. Sample coding according to Table 4.1.

As an interesting element magnesium was found. Even though it is not a regulated element with leaching limits, it is shown in Figure 4.8 due to effectiveness of stabilization materials to this element.

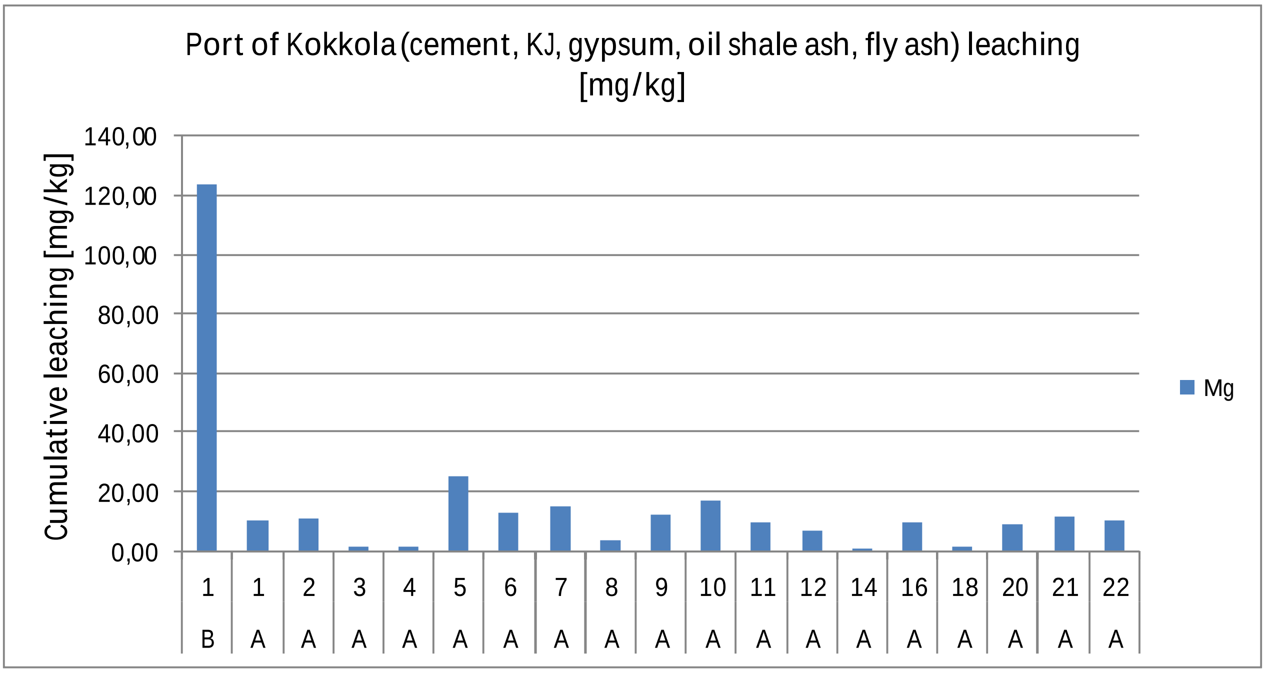

Figure 4.8 Solubility of magnesium (original and stabilized samples). Sediment matrix is from port of Kokkola. Sample coding according to Table 4.1.

In some cases binder materials have been found to increase leaching of nickel. This was found also in the current studies, Figure 4.9. However, the solubilities clearly stay below the limit for common waste (10 mg/kg).

Gypsum can reduce the solubility of some elements. However, it can cause a problem with leaching of sulphate. In all studied cases where gypsum was used, the solubilities exceeded the limit for common waste. In one case, the limit for hazardous waste was exceeded, Figure 4.10. The amount of gypsum applied must be carefully examined and appropriate binder material mixture should include components able to bind releasing sulphate.

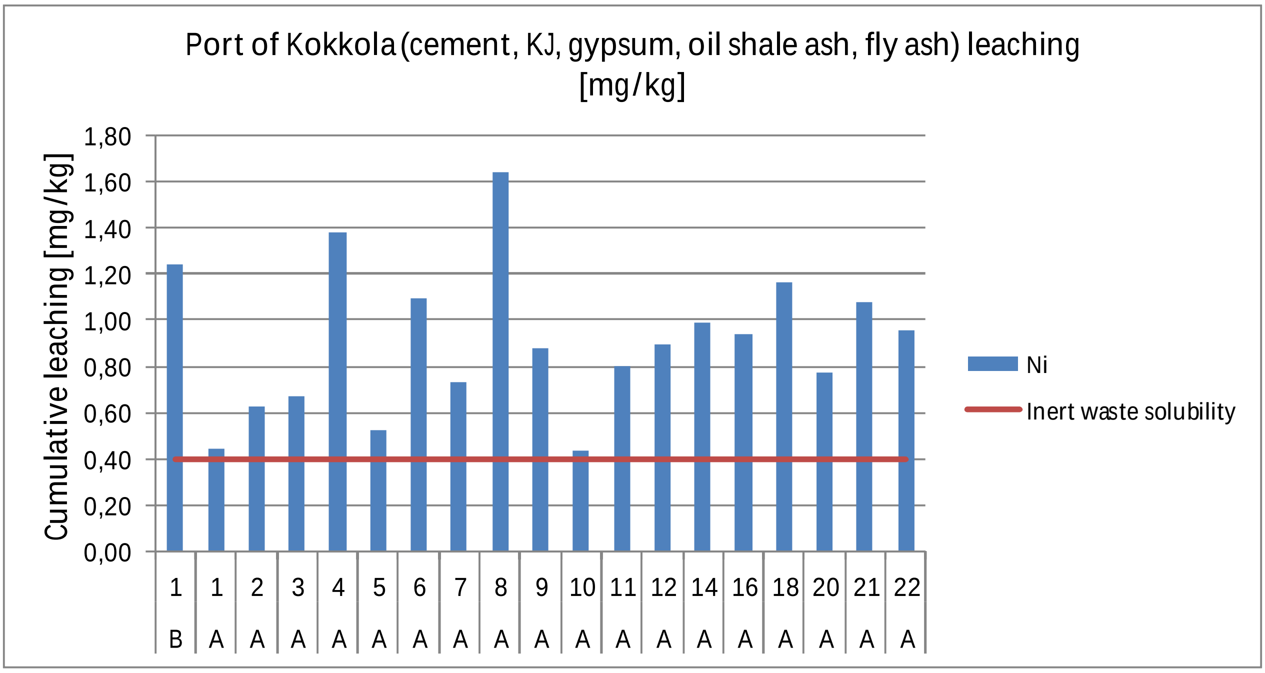

Figure 4.9 Solubility of nickel (original and stabilized samples). Sediment matrix is from port of Kokkola. Sample coding according to Table 4.1.

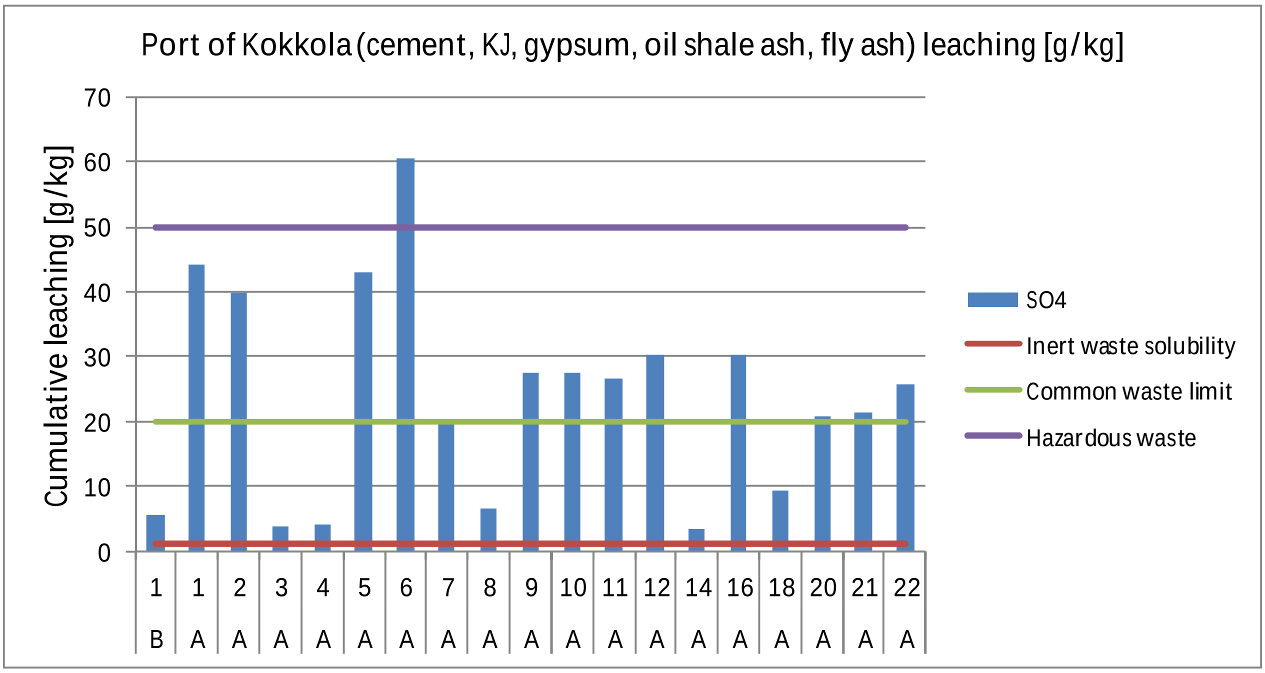

Figure 4.10 Solubility of sulphate (original and stabilized samples). Sediment matrix is from port of Kokkola. Sample coding according to Table 4.1.

4.3 Kymijoki

Samples were collected from river Kymijoki, where a problem has been detected with mercury. This could be well handled with various binder materials. Binder materials are shown in Table 4.2.

Table 4.2 Compositions of experiments following designs of experiments for Kymijoki sediment.

		kg/m^3				
		Fly ash	Oil shale ash	gypsum	slag	cement
B	K	Untreated sample				
A	23	100	0	100	100	100
A	24	0	0	100	100	100
A	25	100	0	0	100	100
A	26	0	0	0	100	100
A	27	100	0	100	0	100
A	28	0	0	100	0	100
A	29	100	0	0	0	100
A	30	0	0	0	0	100
A	31	50	0	50	50	100
A	32	50	0	50	50	100
A	33	50	0	50	50	100
A	34	0	100	100	100	100
A	36	0	100	0	100	100
A	38	0	100	100	0	100
A	40	0	100	0	0	100
A	42	0	50	50	50	100
A	43	0	50	50	50	100

Stabilized samples have all almost the water content. Naturally the amount of binder materials has an effect on the moisture of stabilized material, Figure 4.11.

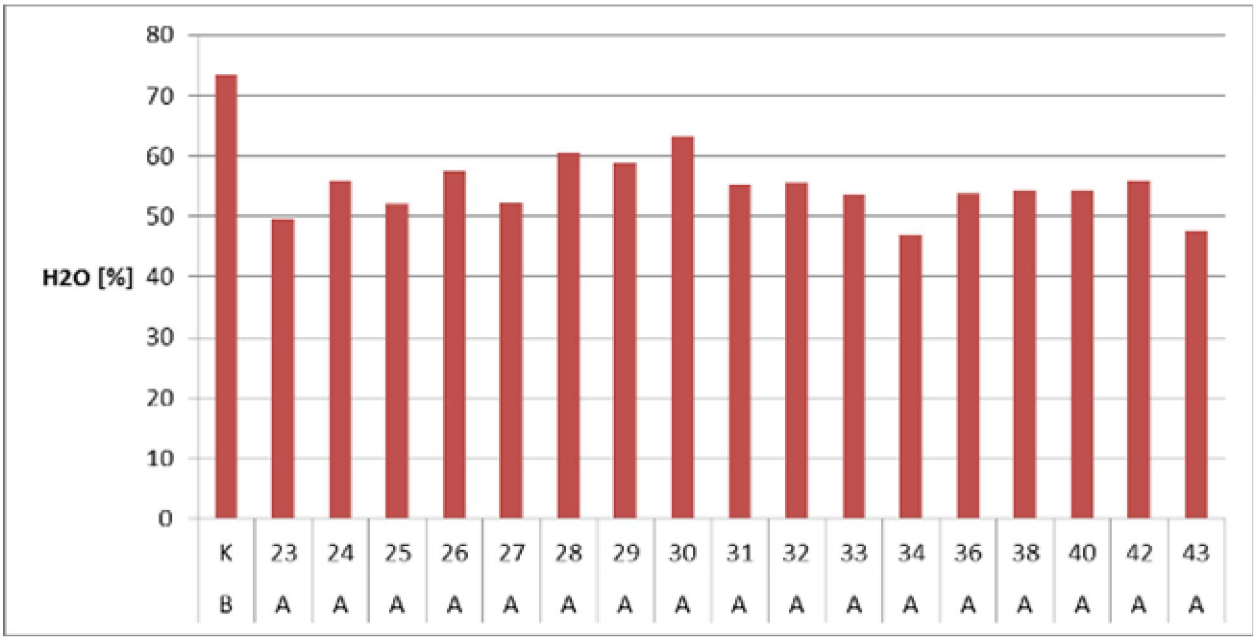

Figure 4.11 Moisture of stabilized samples after stabilization period and prior to batch testing. Sample coding according to Table 4.2.

Measured pH values are close to same of those from diffusion testing indicating large amounts of released base groups that are in equilibrium in the solution, Figure 4.12.

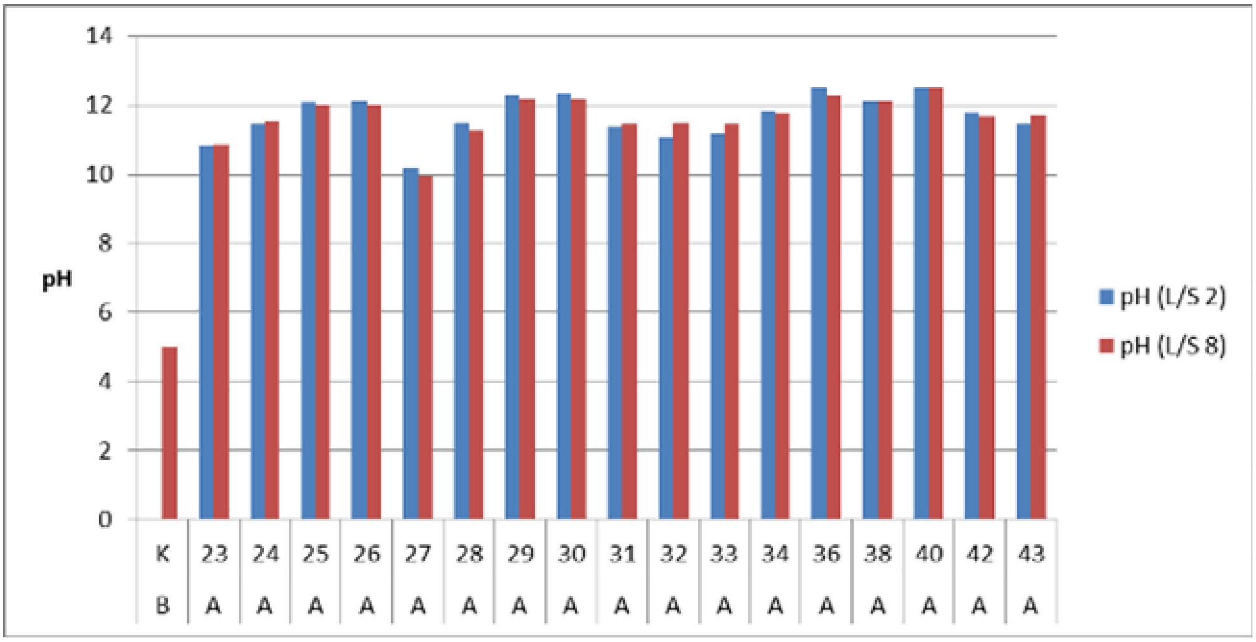

Figure 4.12 Measured pH values from batch testing solution L/S 2 and 8. Sample coding according to Table 4.2.

Almost all selected mixtures resulted in a leaching of mercury less than the limit for inert waste, Figure 4.13.

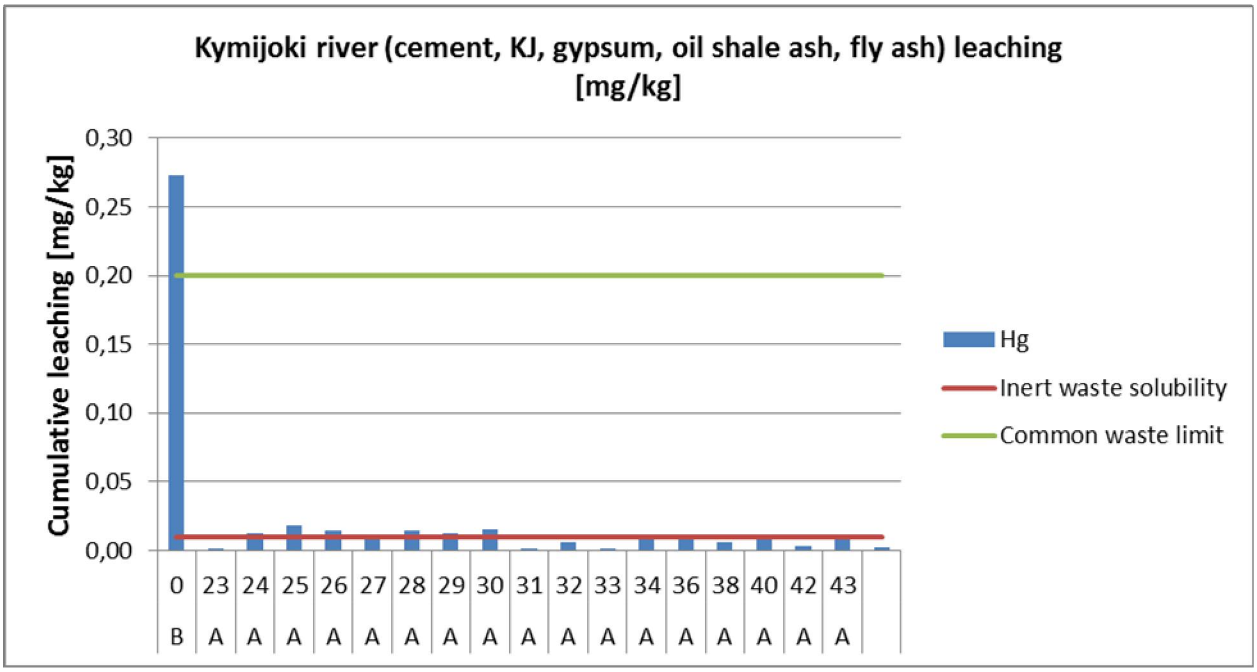

Figure 4.13 Solubility of mercury (original and stabilized samples). Sediment matrix is from river Kymijoki. Sample coding according to Table 4.2.

Similar to the case Port of Kokkola, increased leaching of copper and nickel was found in Kymijoki, Figure 4.14 and Figure 4.15. However, the concentrations are clearly below the limit for common waste for copper (50 mg/kg) and for nickel (10 mg/kg).

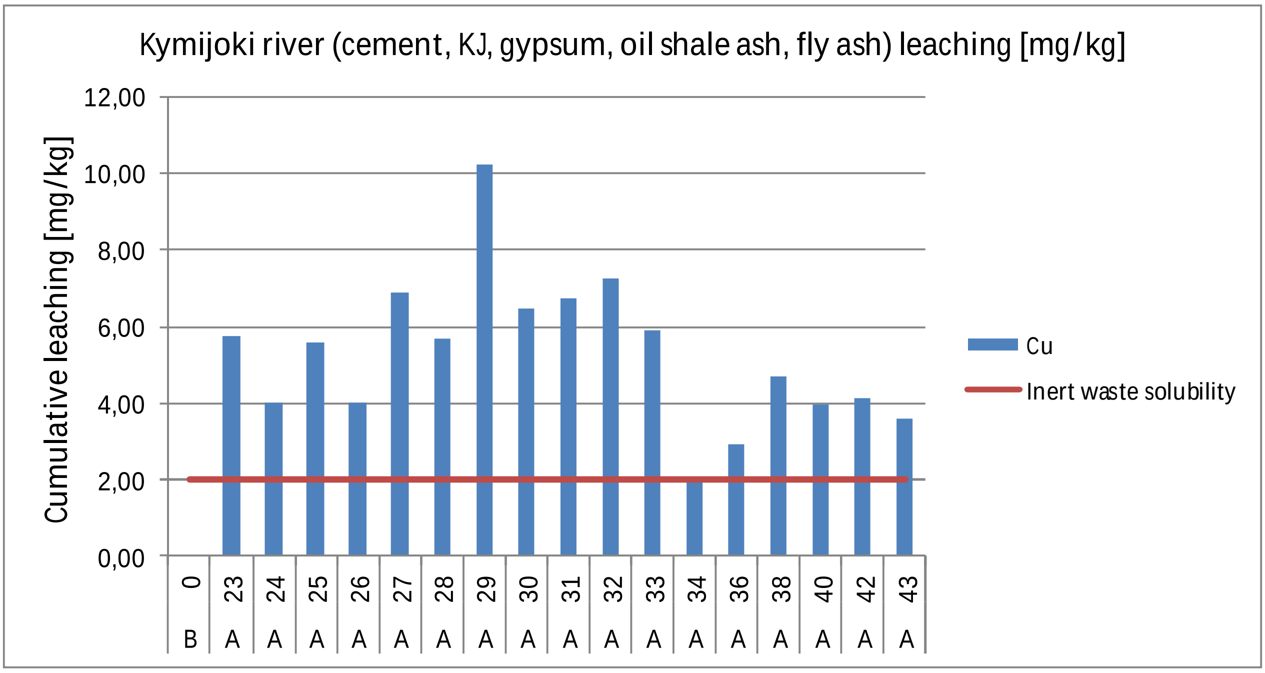

Figure 4.14 Solubility of copper (original and stabilized samples). Sediment matrix is from river Kymijoki. Sample coding according to Table 4.2.

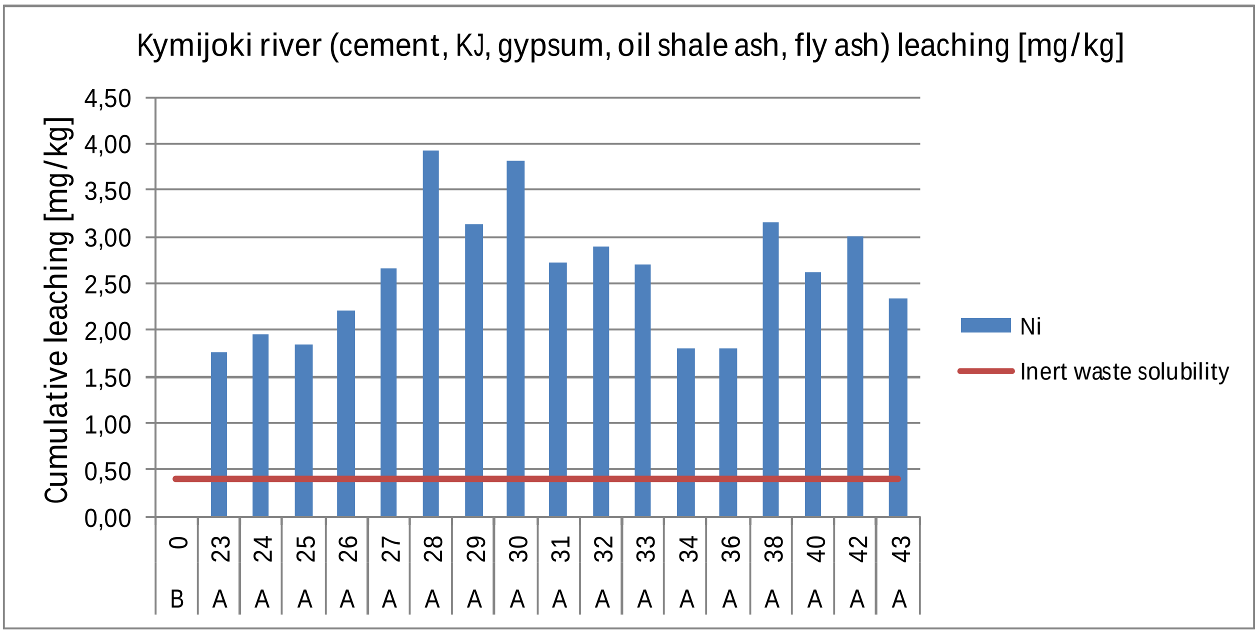

Figure 4.15 Solubility of nickel (original and stabilized samples). Sediment matrix is from river Kymijoki. Sample coding according to Table 4.2.

Care should be taken with amounts of gypsum. Similar to the Port of Kokkola case, here also addition of gypsum can lead to large emissions of sulphate, Figure 4.16.

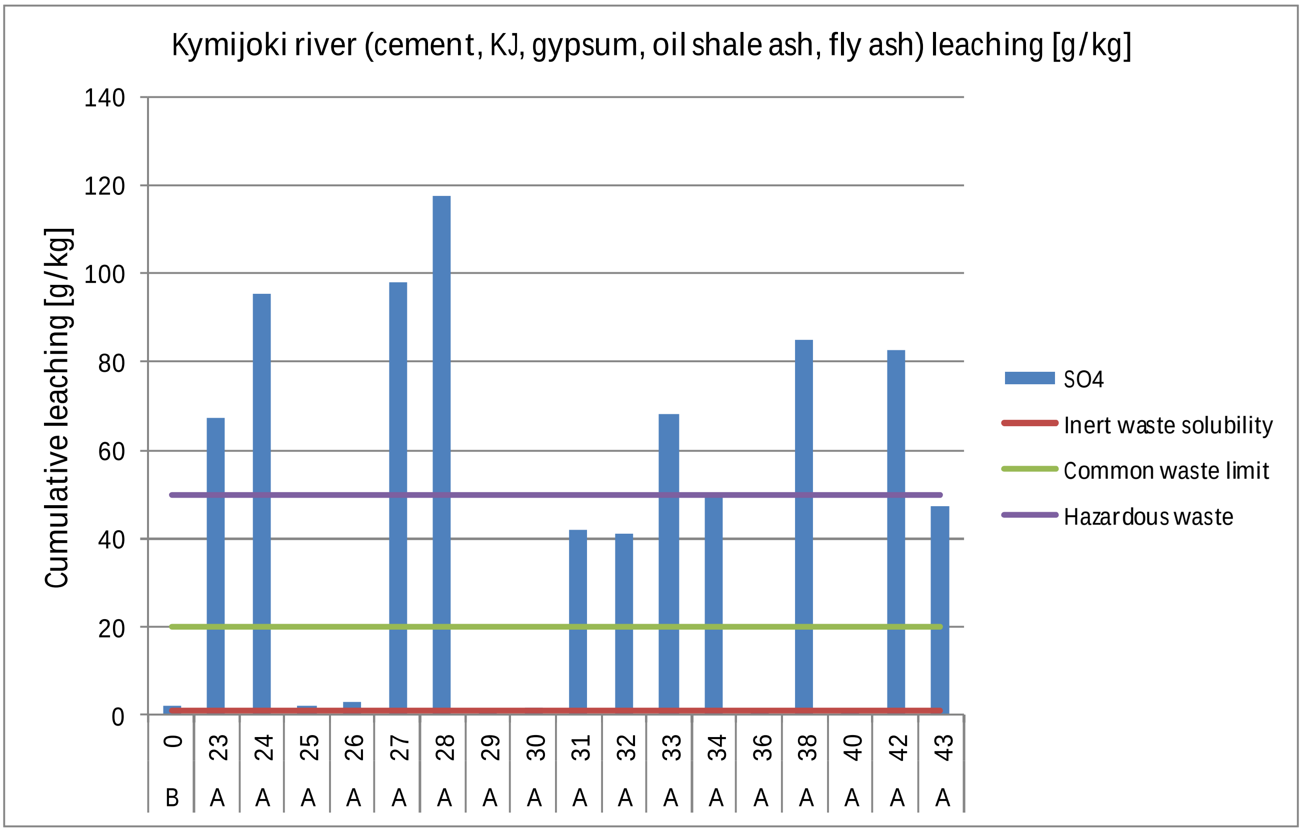

Figure 4.16 Solubility of sulphate (original and stabilized samples). Sediment matrix is from river Kymijoki. Sample coding according to Table 4.2.

4.4 Port of Gävle

Samples from Port of Gävle were stabilized as shown in Table 4.3.

Table 4.3 Compositions of experiments following designs of experiments for Gävle sediment.

		[kg/m^3]				
		Fly ash	Oil shale ash	gypsum	slag	cement
B	G	Untreated sample				
D	1	50	0	25	25	50
D	2	50	0	25	0	50
D	3	0	0	25	25	50
D	4	0	0	25	0	50
D	5	50	0	0	25	50
D	6	50	0	0	0	50
D	7	0	0	0	25	50
D	8	0	0	0	0	50
D	9	25	0	12,5	12,5	50
D	10	0	50	0	25	50
D	11	0	50	0	0	50
D	12	0	0	0	25	50
D	13	0	0	0	0	50
D	14	0	25	0	12,5	50

Water content of stabilized samples is quite similar to that of original unstabilized sample, Figure 4.17.

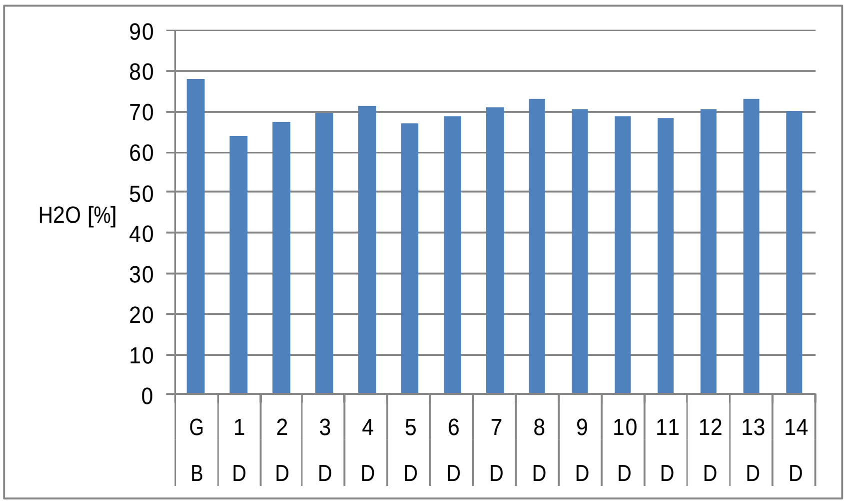

Figure 4.17 Water content of stabilized samples (Port of Gävle matrix). Sample coding according to Table 4.3.

Measured pH values from batch test solutions are shown in Figure 4.18.

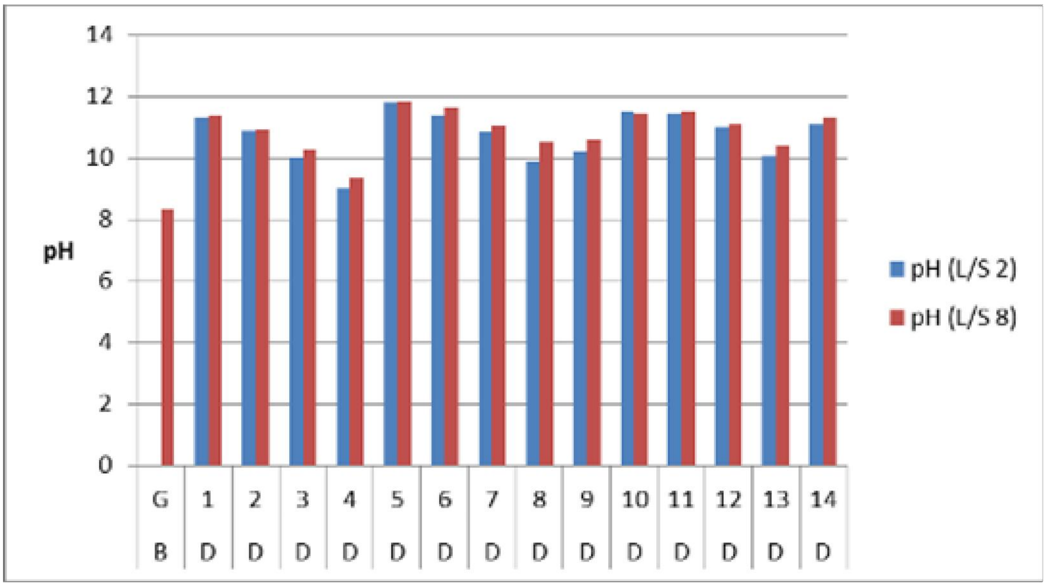

Figure 4.18 pH values of Port of Gävle samples batch testing. Sample coding according to Table 4.3.

Cumulative leaching concentrations are shown in Figures 4.19 -4.31.

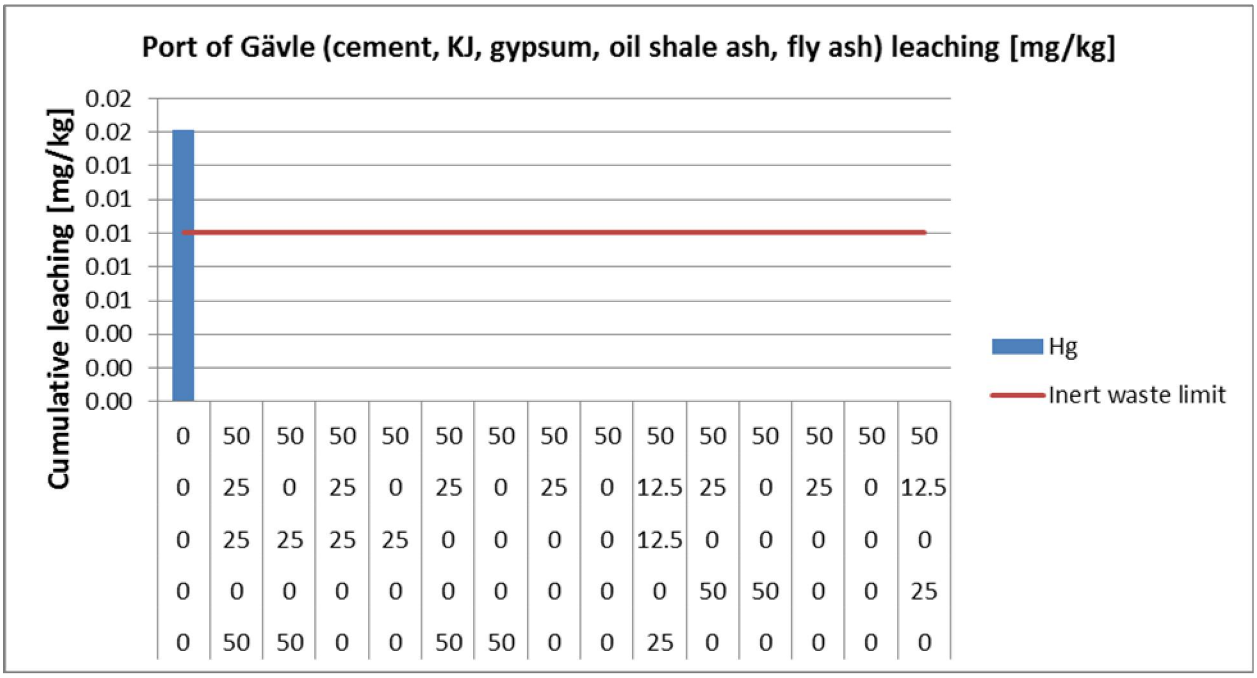

Figure 4.19 Solubility of mercury (original and stabilized samples). Sediment matrix is from Port of Gävle. Sample coding according to Table 4.3.

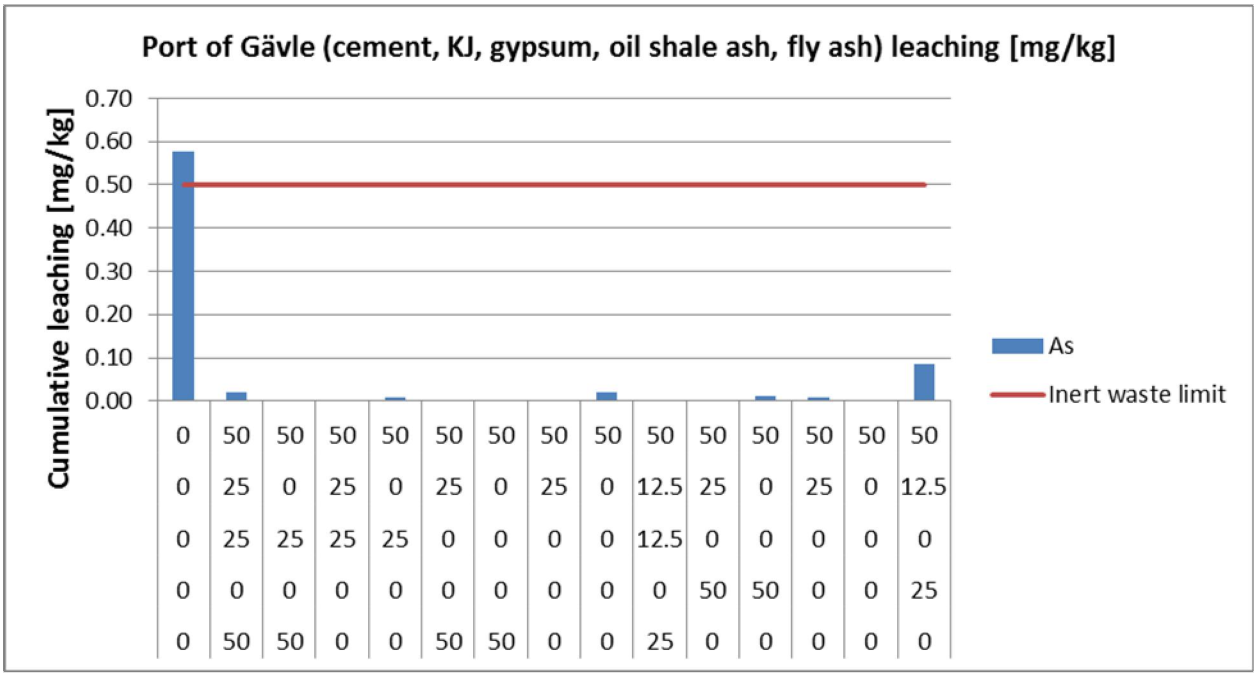

Figure 4.20 Solubility of arsenic (original and stabilized samples). Sediment matrix is from Port of Gävle. Sample coding according to Table 4.3.

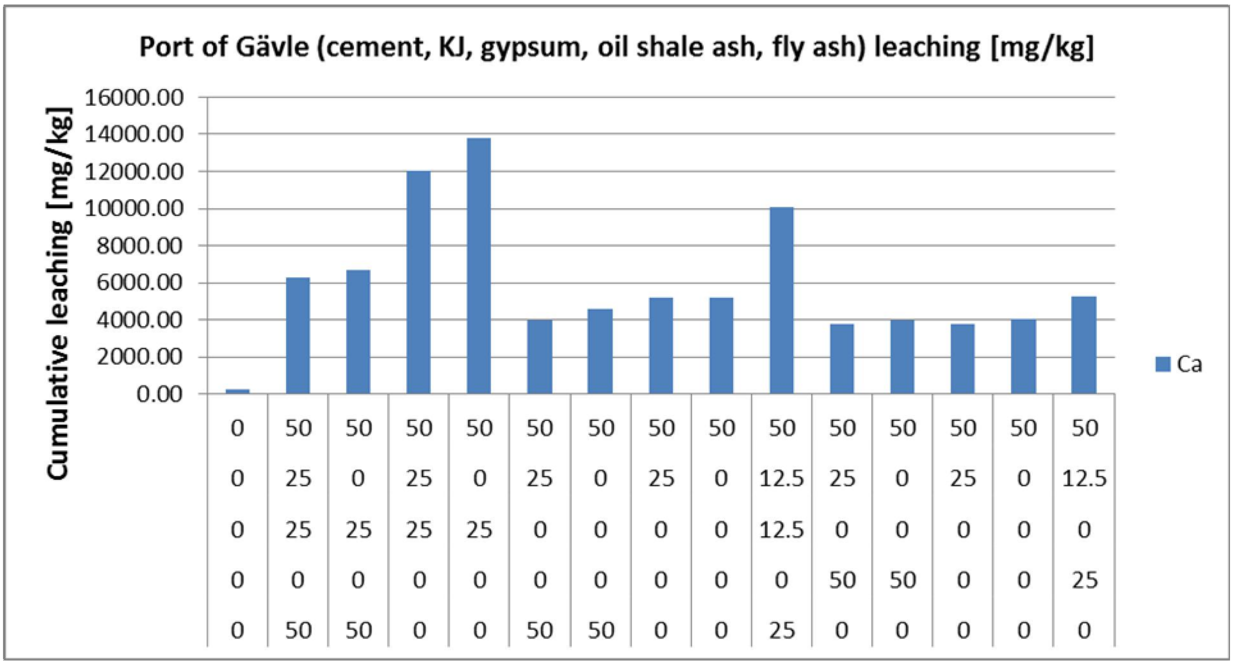

Figure 4.21 Solubility of calcium (original and stabilized samples). Sediment matrix is from Port of Gävle. Sample coding according to Table 4.3.

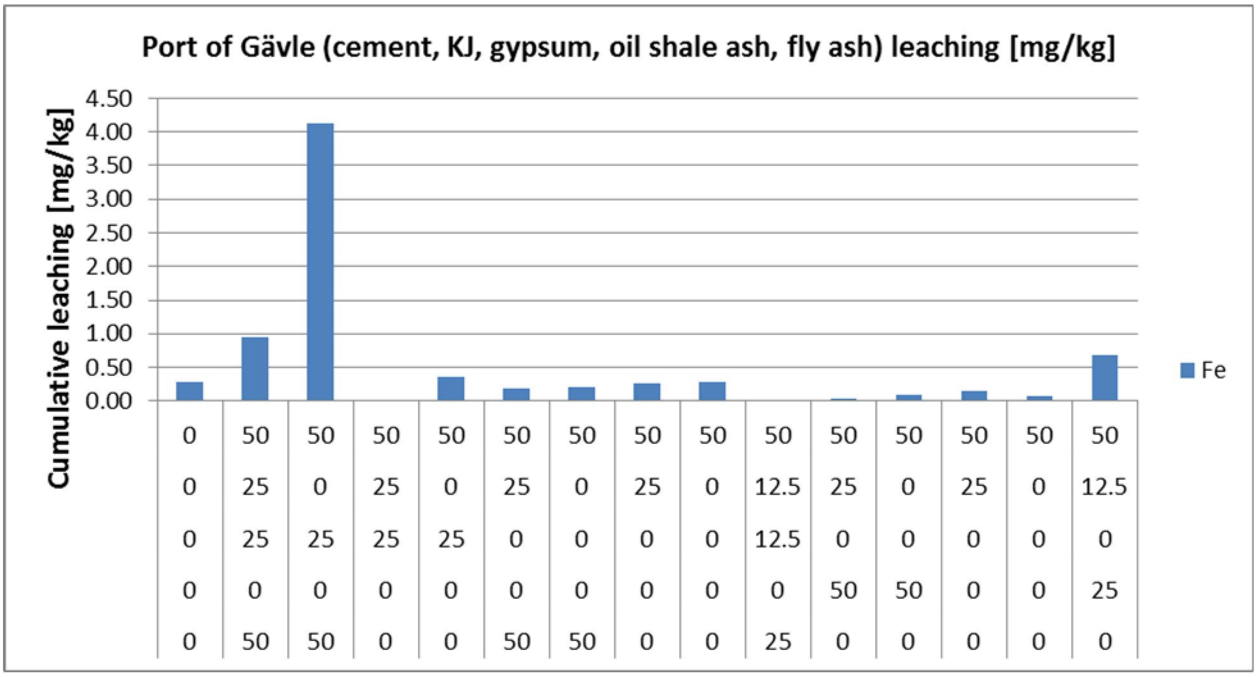

Figure 4.22 Solubility of iron (original and stabilized samples). Sediment matrix is from Port of Gävle. Sample coding according to Table 4.3.

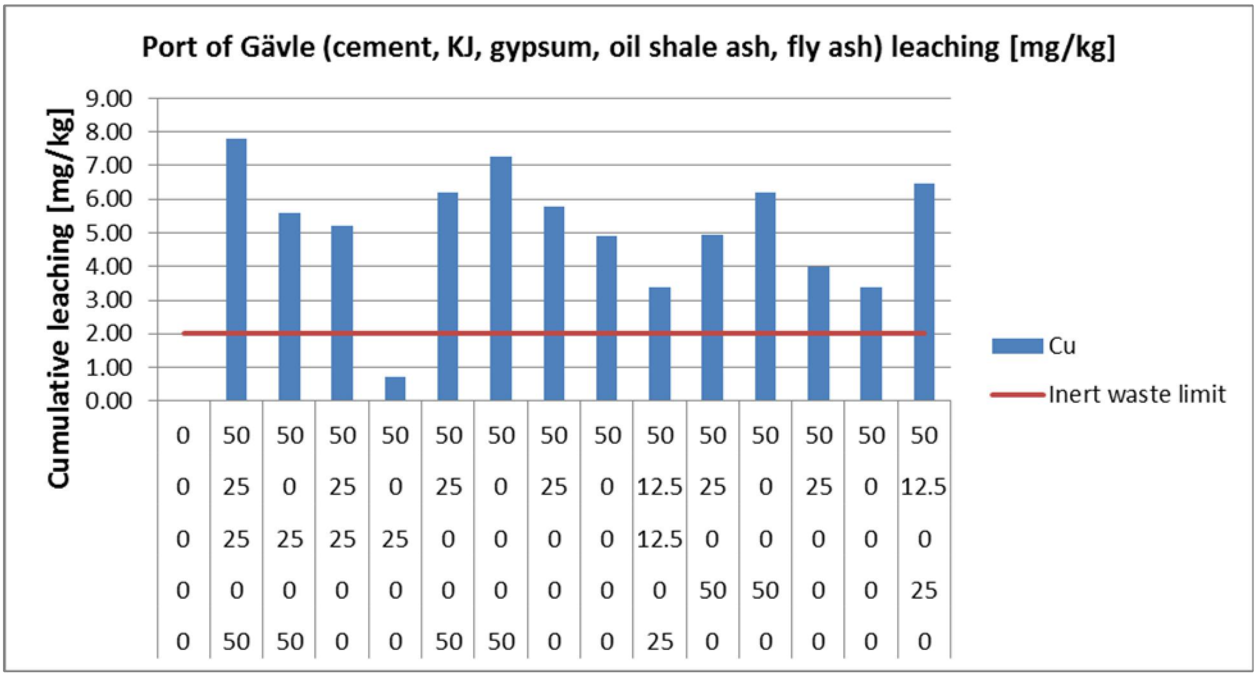

Figure 4.23 Solubility of copper (original and stabilized samples). Sediment matrix is from Port of Gävle. Sample coding according to Table 4.3.

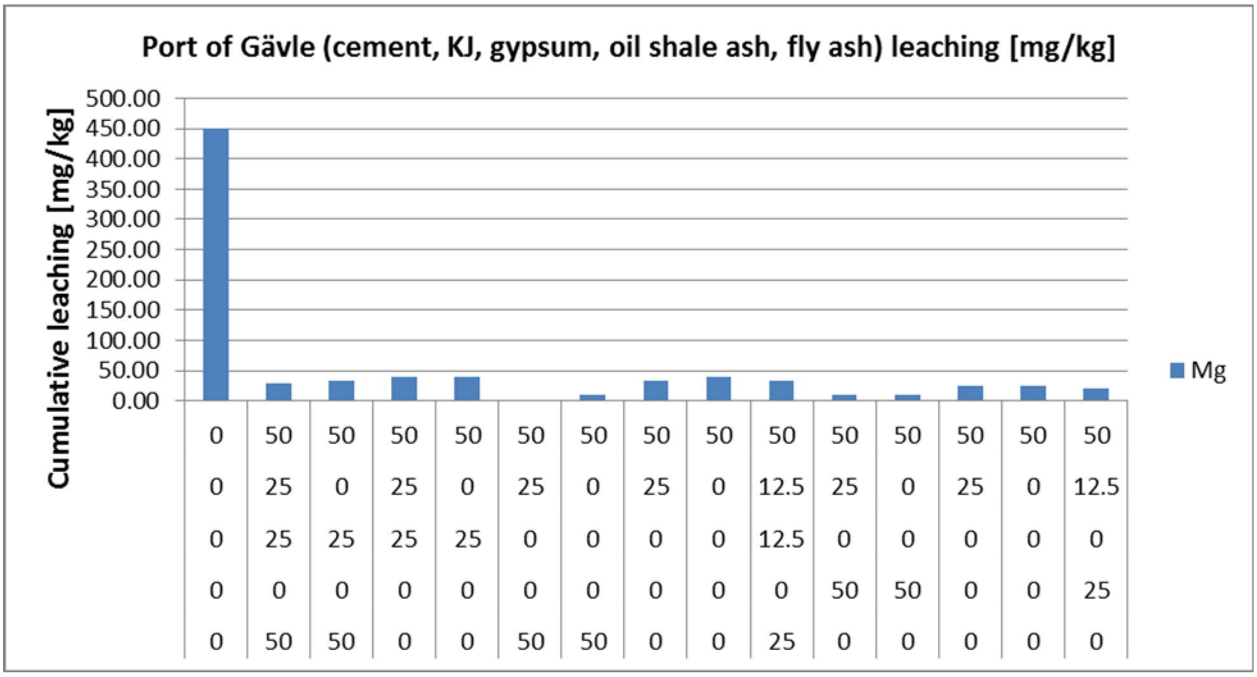

Figure 4.24 Solubility of magnesium (original and stabilized samples). Sediment matrix is from Port of Gävle. Sample coding according to Table 4.3.

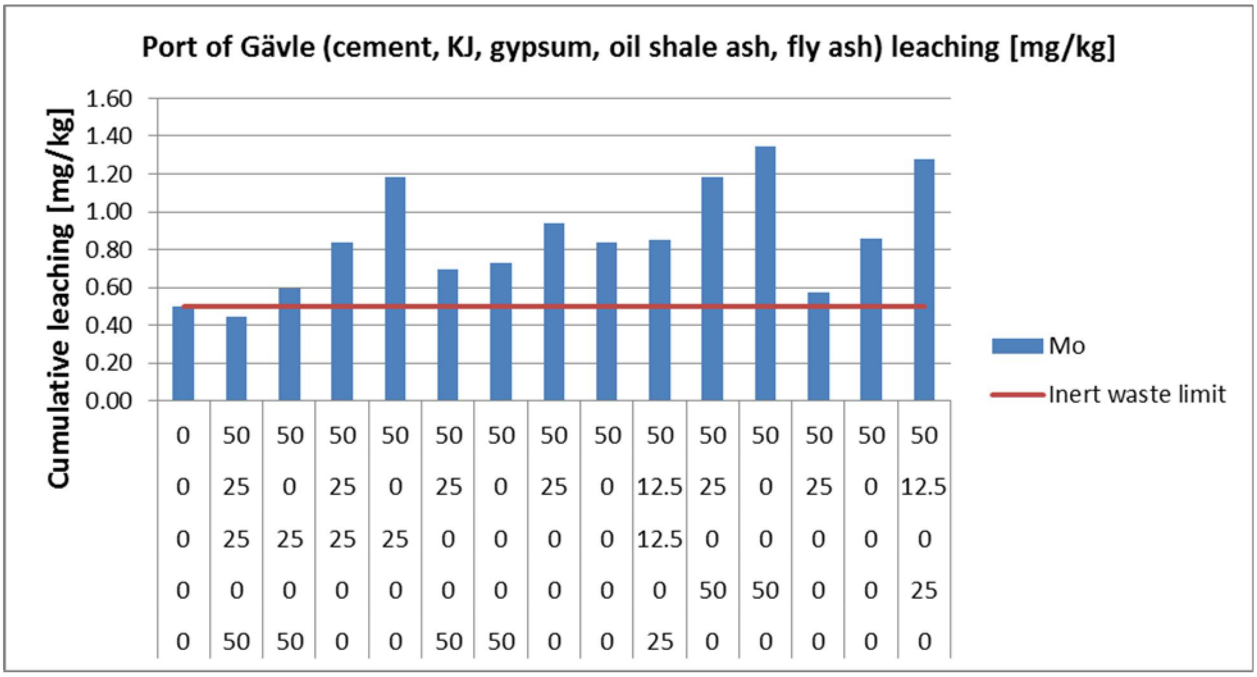

Figure 4.25 Solubility of molybdenum (original and stabilized samples). Sediment matrix is from Port of Gävle. Sample coding according to Table 4.3.

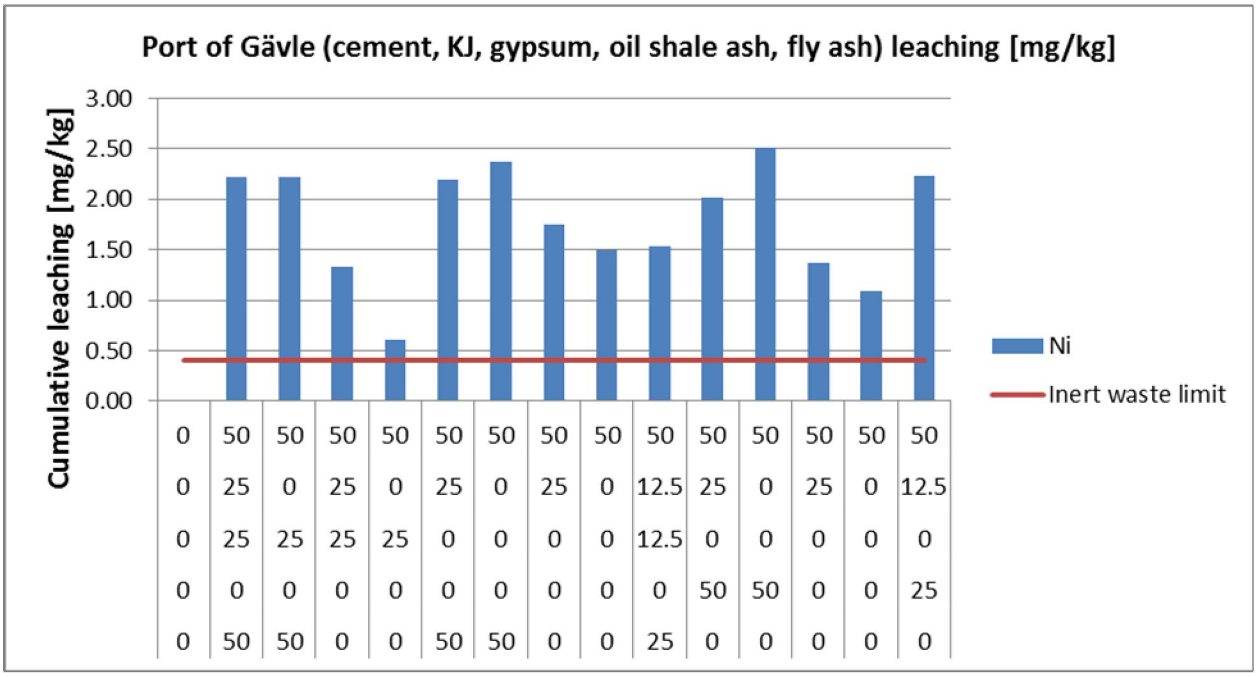

Figure 4.26 Solubility of nickel (original and stabilized samples). Sediment matrix is from Port of Gävle. Sample coding according to Table 4.3.

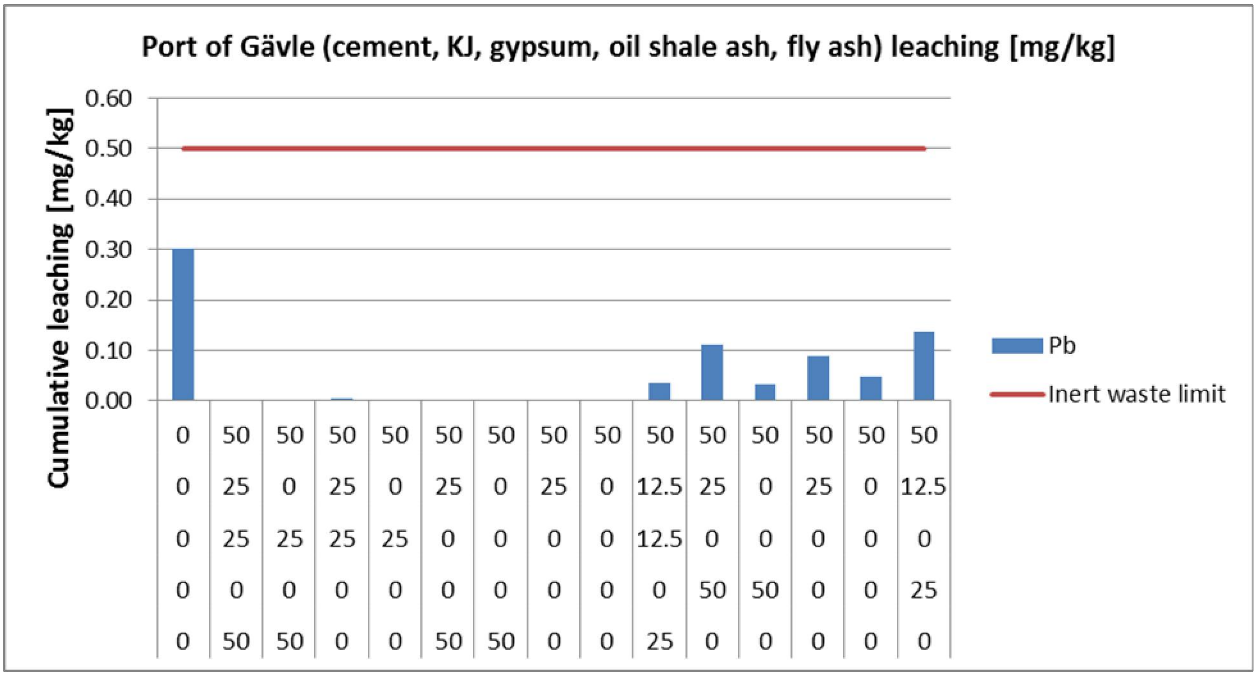

Figure 4.27 Solubility of lead (original and stabilized samples). Sediment matrix is from Port of Gävle. Sample coding according to Table 4.3.

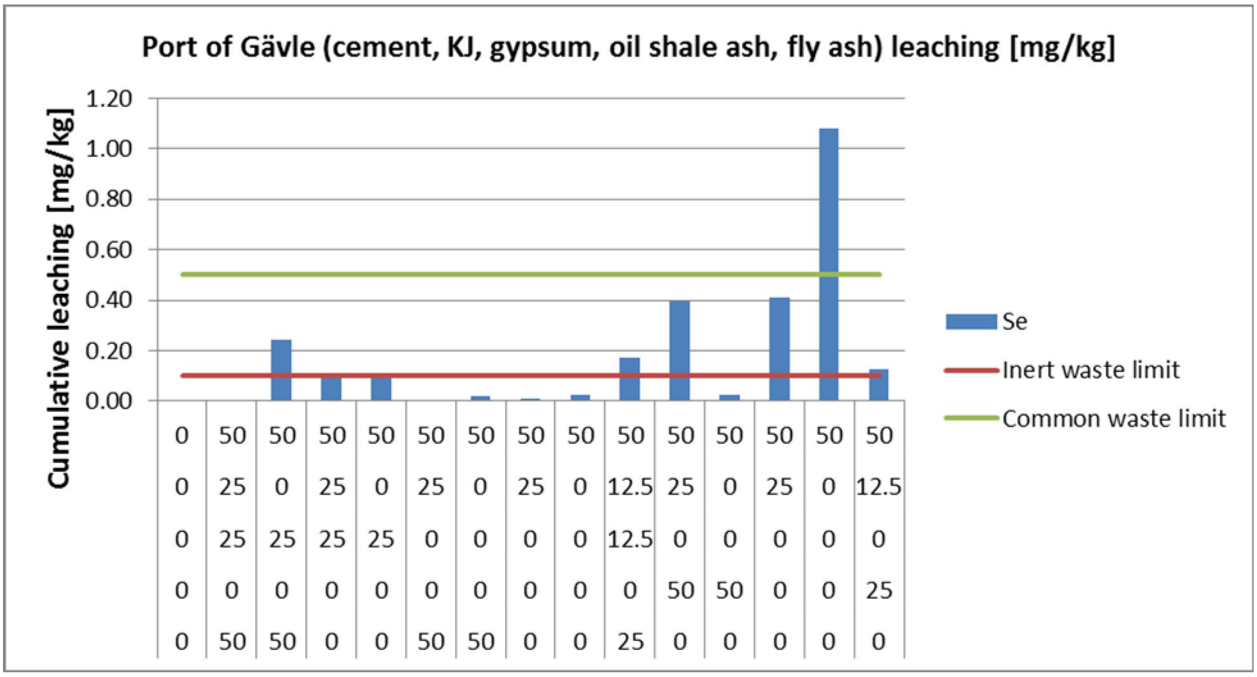

Figure 4.28 Solubility of selenium (original and stabilized samples). Sediment matrix is from Port of Gävle. Sample coding according to Table 4.3.

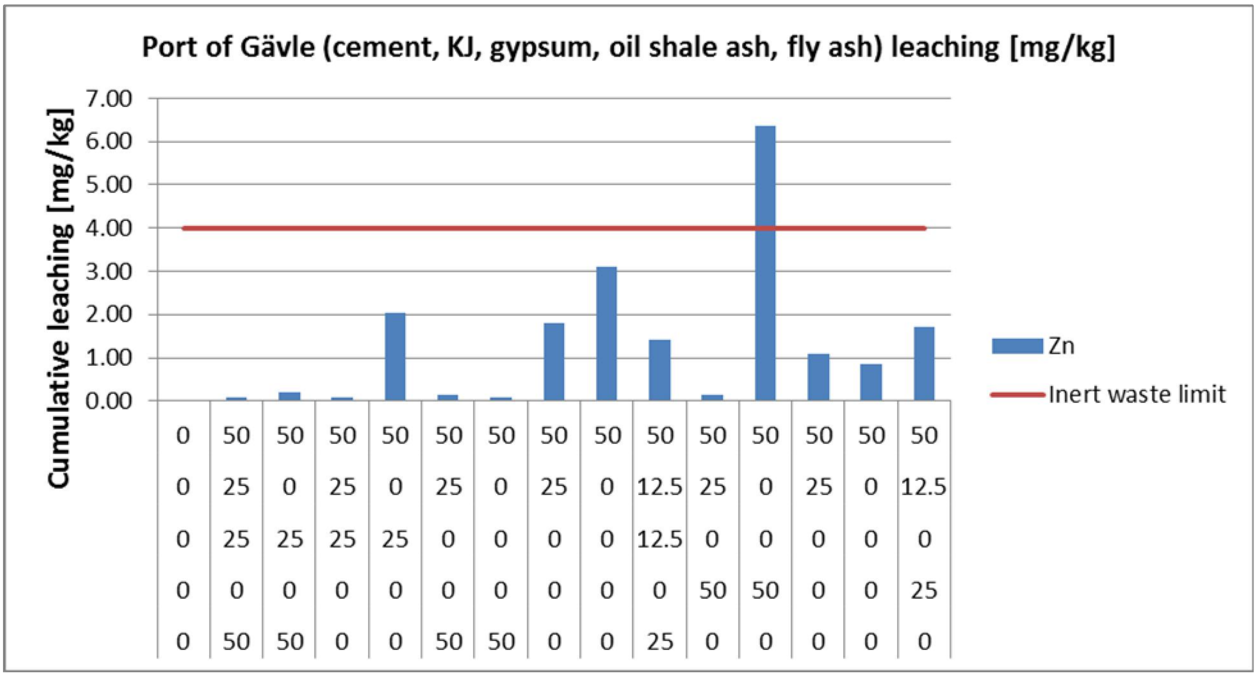

Figure 4.29 Solubility of zinc (original and stabilized samples). Sediment matrix is from Port of Gävle. Sample coding according to Table 4.3.

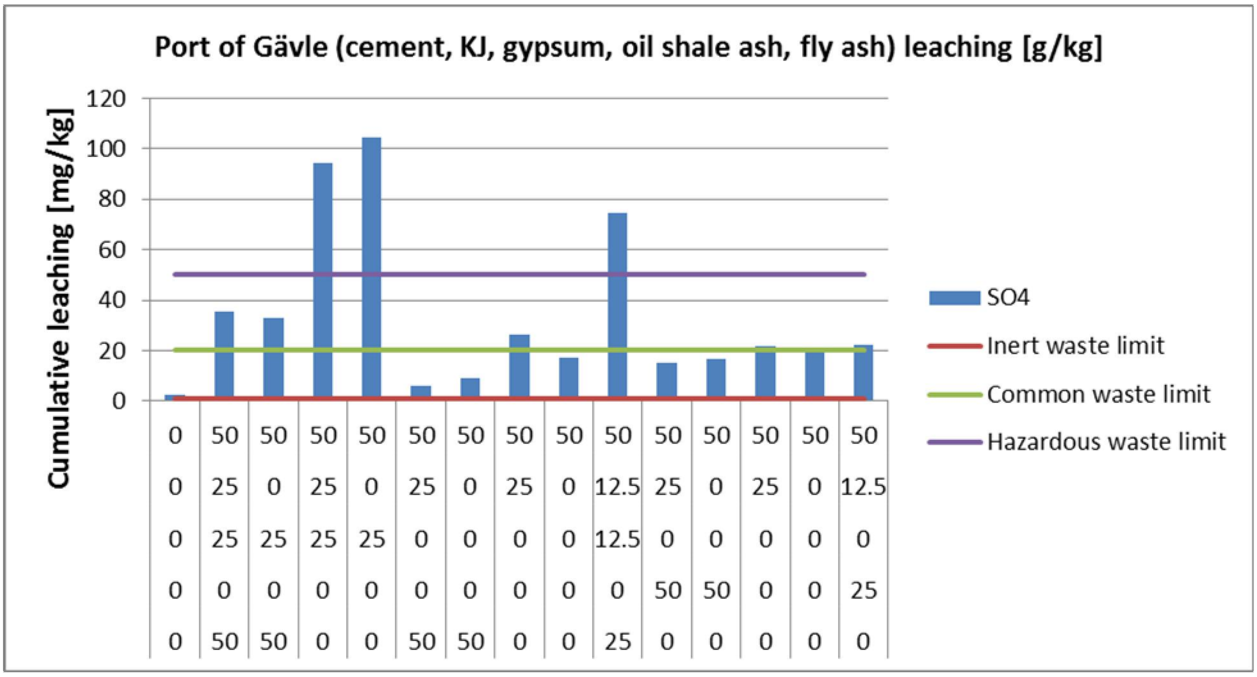

Figure 4.30 Solubility of sulphate (original and stabilized samples). Sediment matrix is from Port of Gävle. Sample coding according to Table 4.3.

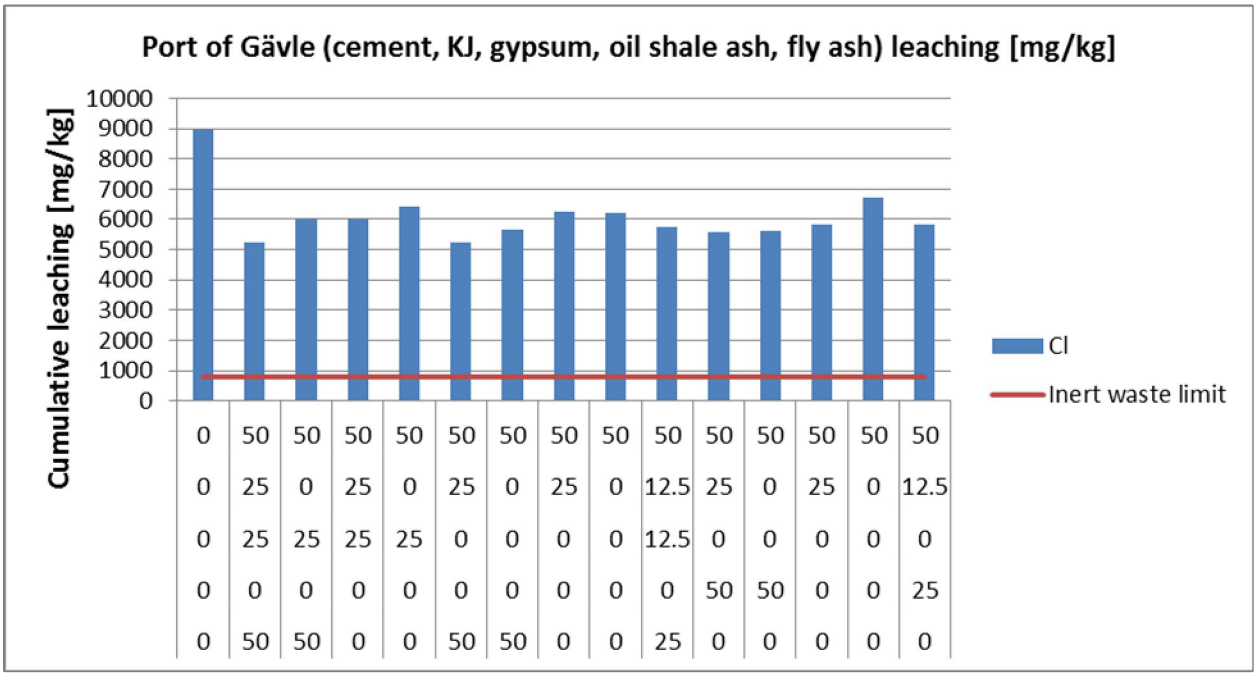

Figure 4.31 Solubility of chloride (original and stabilized samples). Sediment matrix is from Port of Gävle. Sample coding according to Table 4.3.

4.5 Diffusion test leaching

64 days diffusion testing was used to test leaching of elements and compounds from monolithic material. pH value was set to 4 with nitric acid and water was changed after 1, 4, 16 and 64 days. Figure 4.32 shows the measured leached calcium concentration in mg/m^2 units.

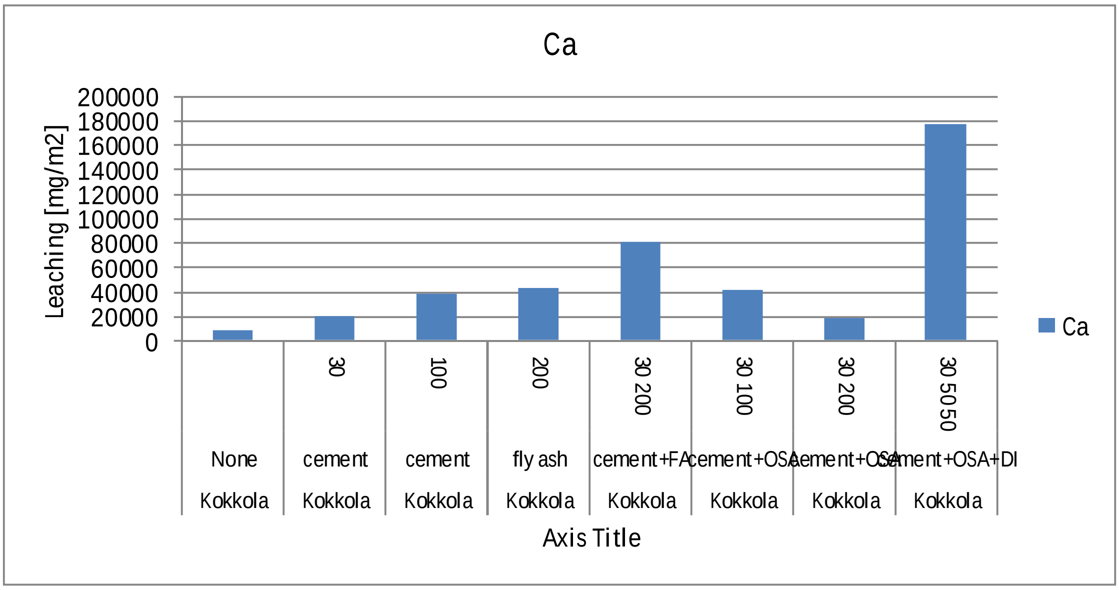

Figure 4.32 Solubility of calcium (original and stabilized samples). Sediment matrix is from Port of Kokkola.

The leaching of iron is easily reduced by stabilization, Figure 4.33.

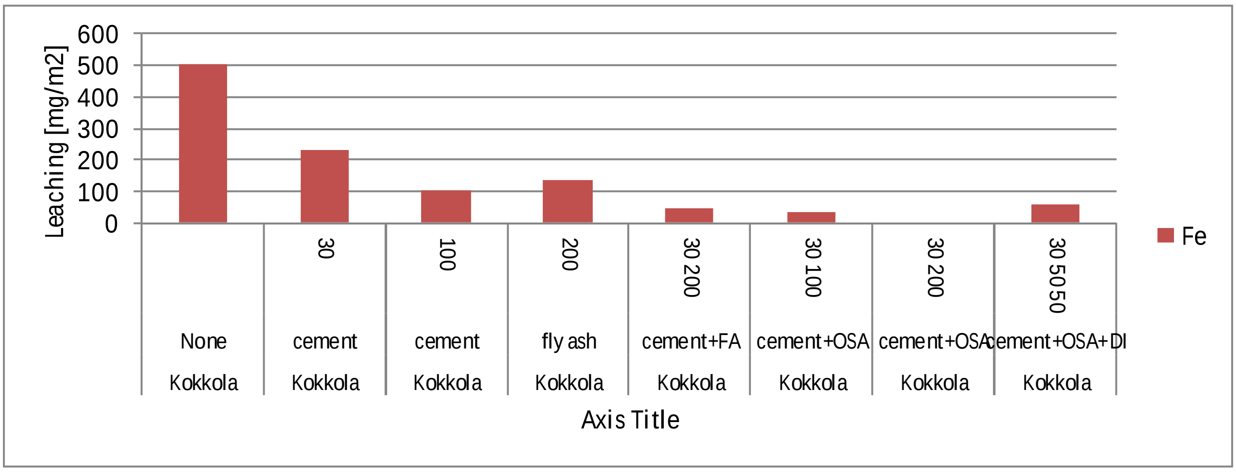

Figure 4.33 Cumulative leaching of iron (original and stabilized samples). Sediment matrix is from Port of Kokkola.

Cumulative leaching of magnesium appears to increase with increasing amounts of binder materials unless they react with each other, Figure 4.34.

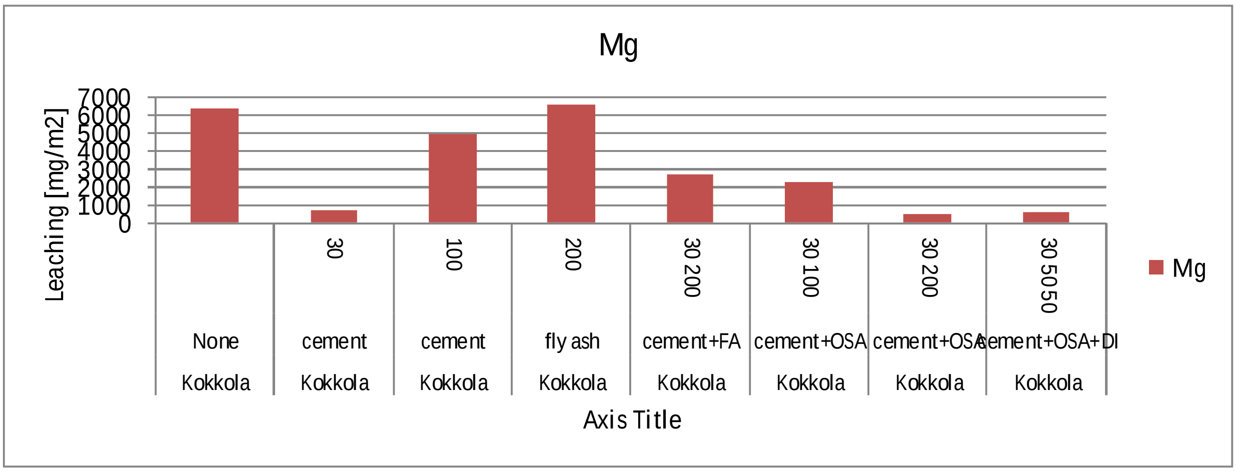

Figure 4.34 Cumulative leaching of magnesium (original and stabilized samples). Sediment matrix is from Port of Kokkola.

Cumulative leaching of nickel is shown in Figure 4.35. It seems that various components may increase the leaching of nickel.

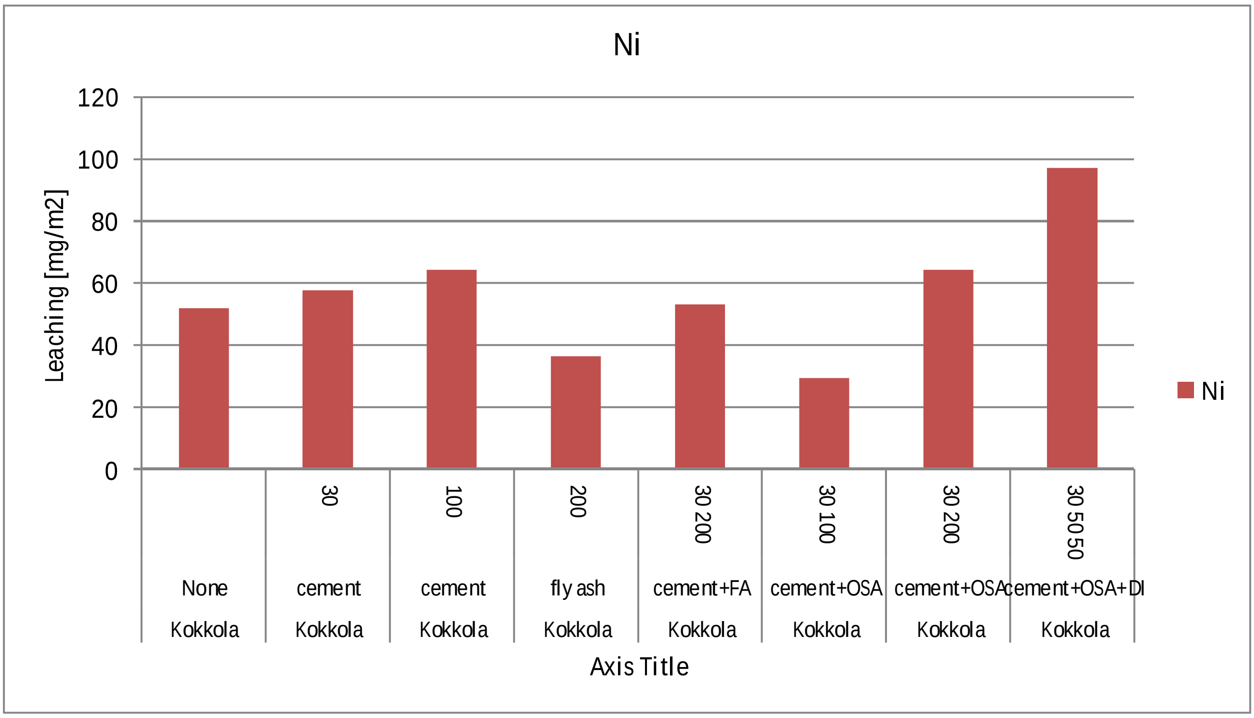

Figure 4.35 Cumulative leaching of nickel (original and stabilized samples). Sediment matrix is from Port of Kokkola.

Strontium appears only when gypsum has been used as a binder material, Figure 4.36. Other amounts are low. However, since only one sample contains gypsum, conclusions cannot be done.

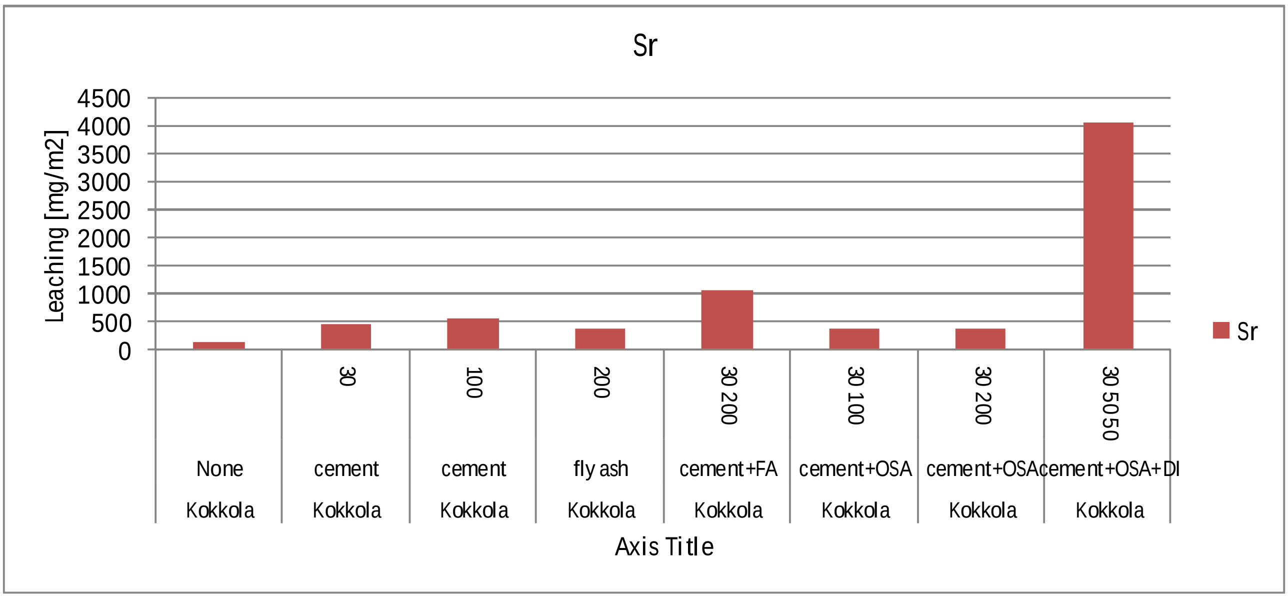

Figure 4.36 Cumulative leaching of strontium (original and stabilized samples). Sediment matrix is from Port of Kokkola.

One major contaminant in Port of Kokkola is zinc. Cumulative diffusion leaching can be effectively reduced with all studied mixtures except only fly ash, Figure 4.37.

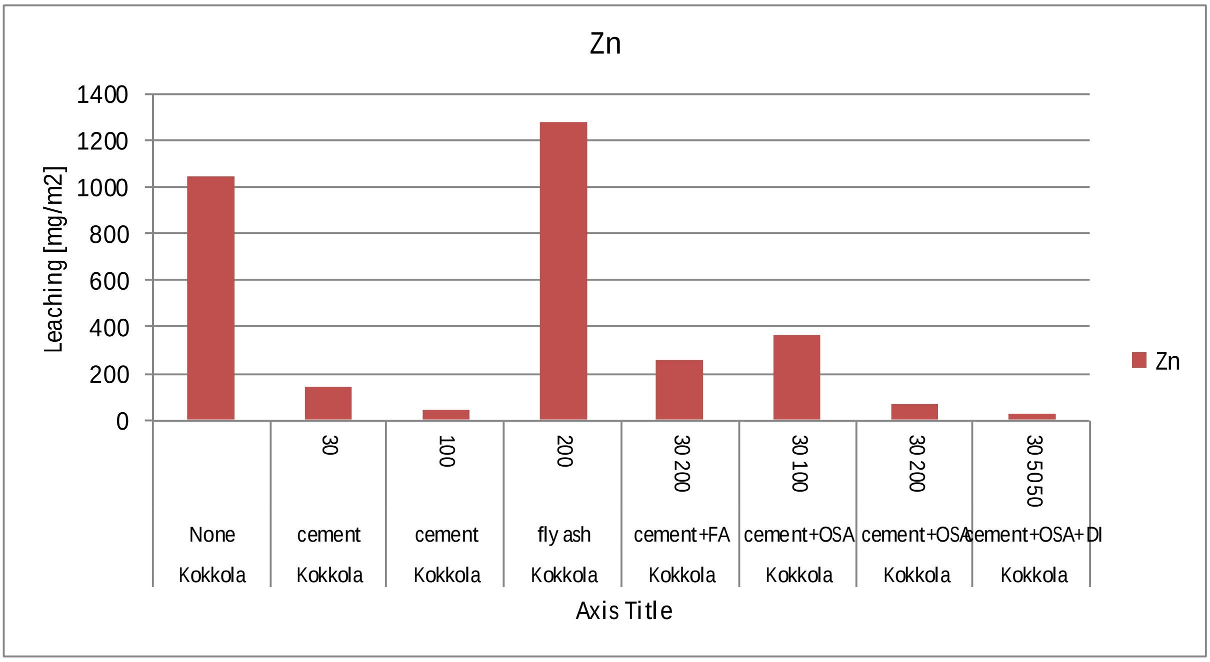

Figure 4.37 Cumulative leaching of zinc (original and stabilized samples). Sediment matrix is from Port of Kokkola.

Studies with Kymijoki matrix give similar results on strontium than Port of Kokkola. However, elevated concentrations were found on more binder mixtures, Figure 4.38.

Increased nickel concentrations can be seen, especially with high binder amounts, Figure 4.39.

Magnesium has basically no diffusion leaching from stabilized Kymijoki sediment, Figure 4.40.

The diffusion release of potassium seems to increase with high amounts of binder materials, Figure 4.41.

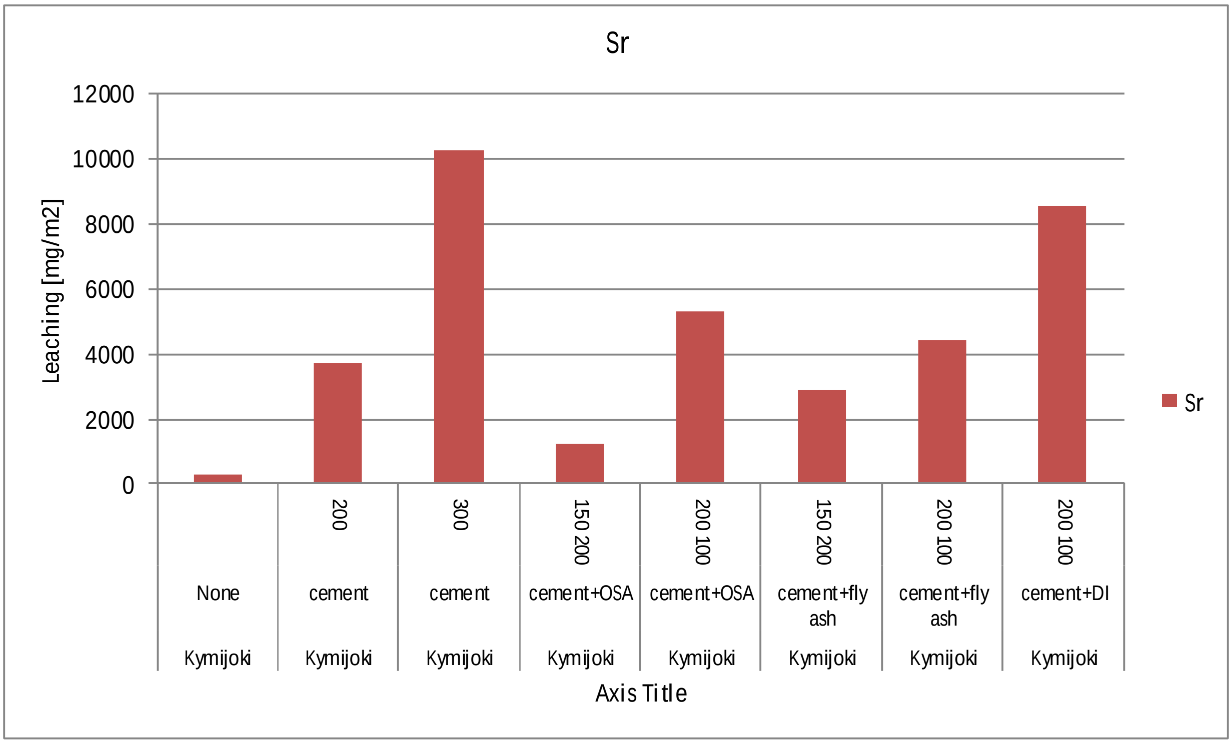

Figure 4.38 Cumulative leaching of strontium (original and stabilized samples). Sediment matrix is from river Kymijoki.

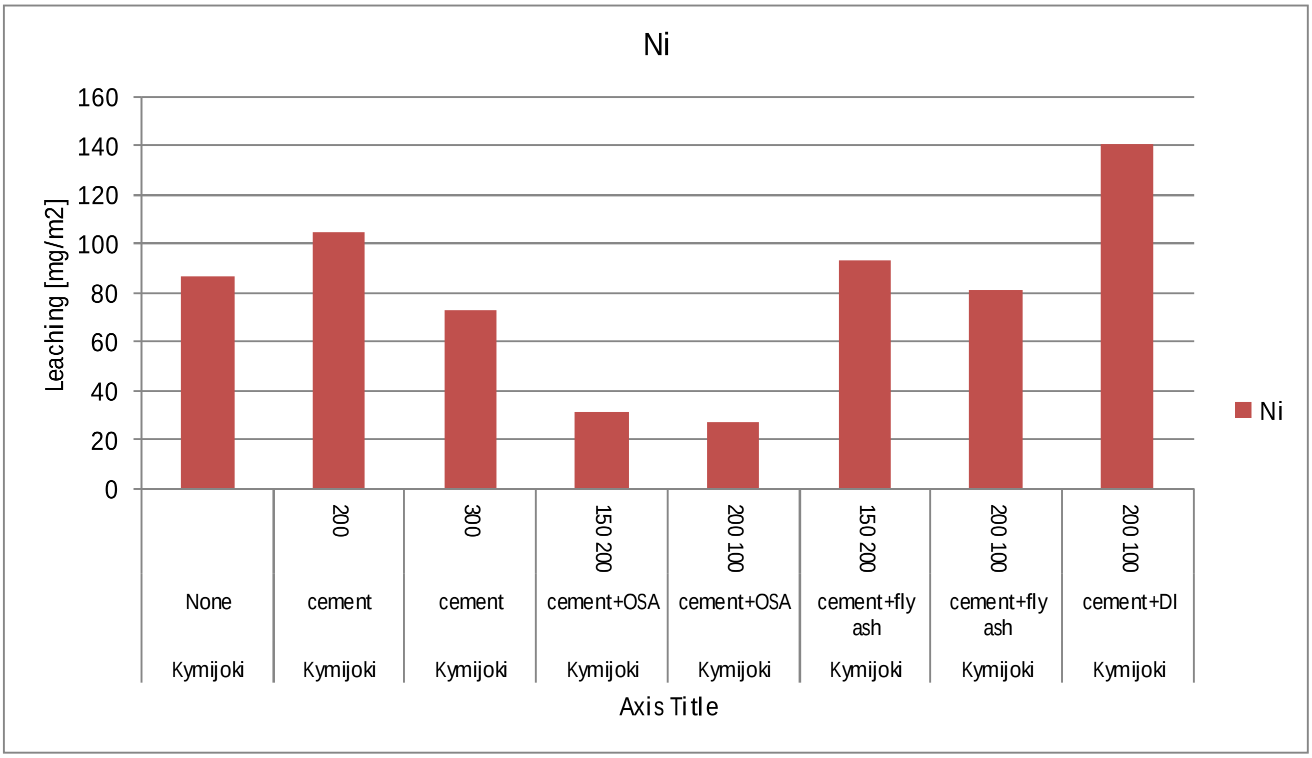

Figure 4.39 Cumulative leaching of nickel (original and stabilized samples). Sediment matrix is from river Kymijoki.

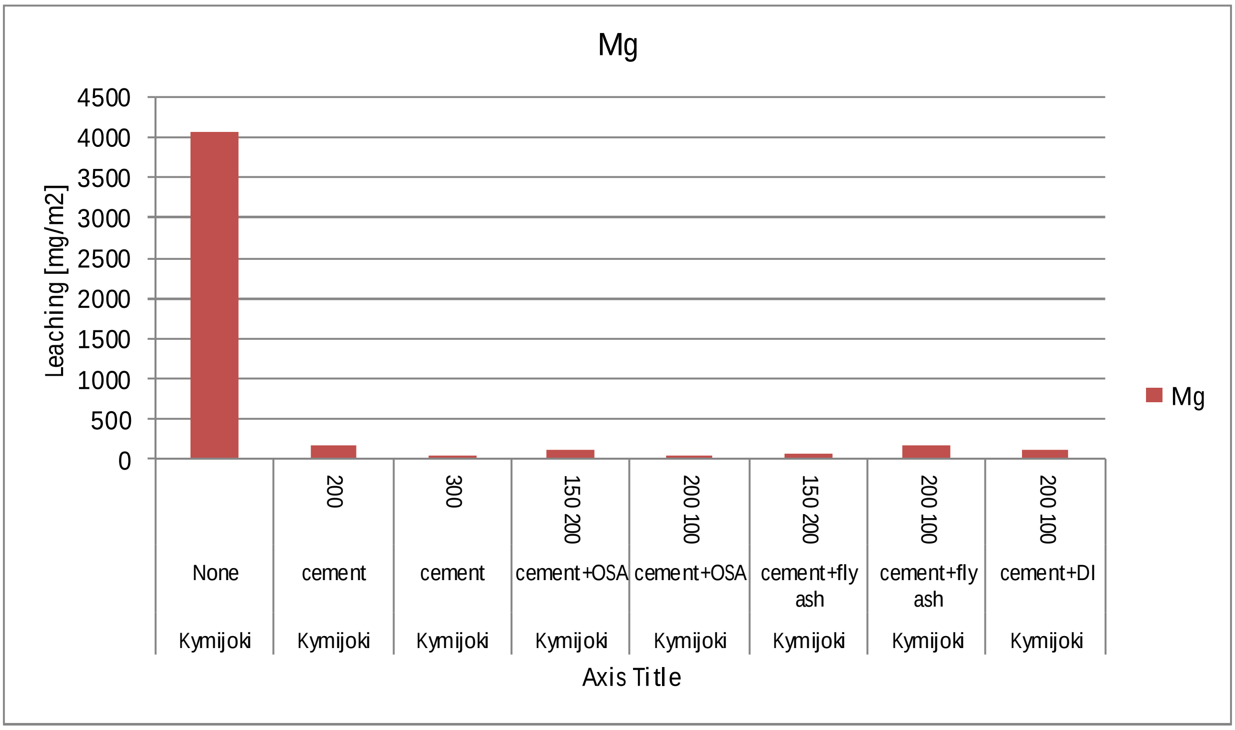

Figure 4.40 Cumulative leaching of magnesium (original and stabilized samples). Sediment matrix is from river Kymijoki.

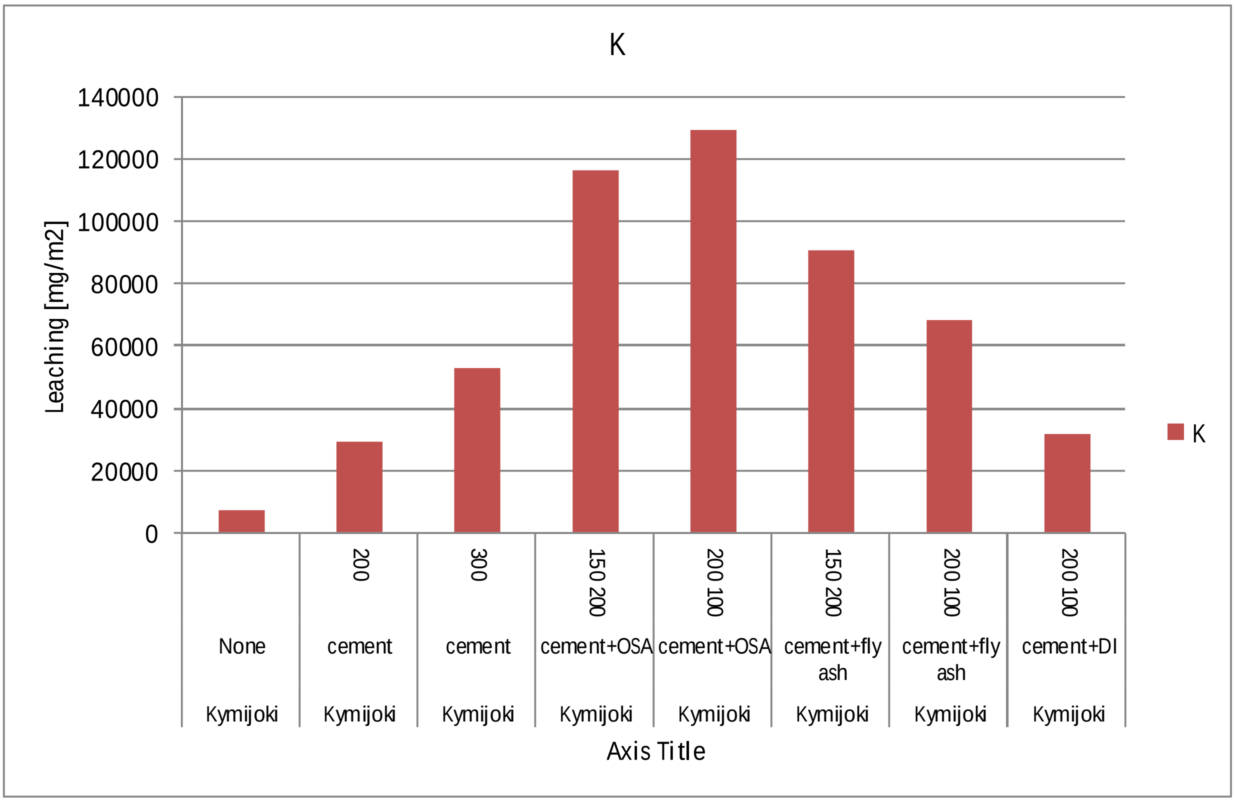

Figure 4.41 Cumulative leaching of potassium (original and stabilized samples). Sediment matrix is from river Kymijoki.

Excessive amounts of cement can be detected from increased values of diffused calcium leaching, Figure 4.42.

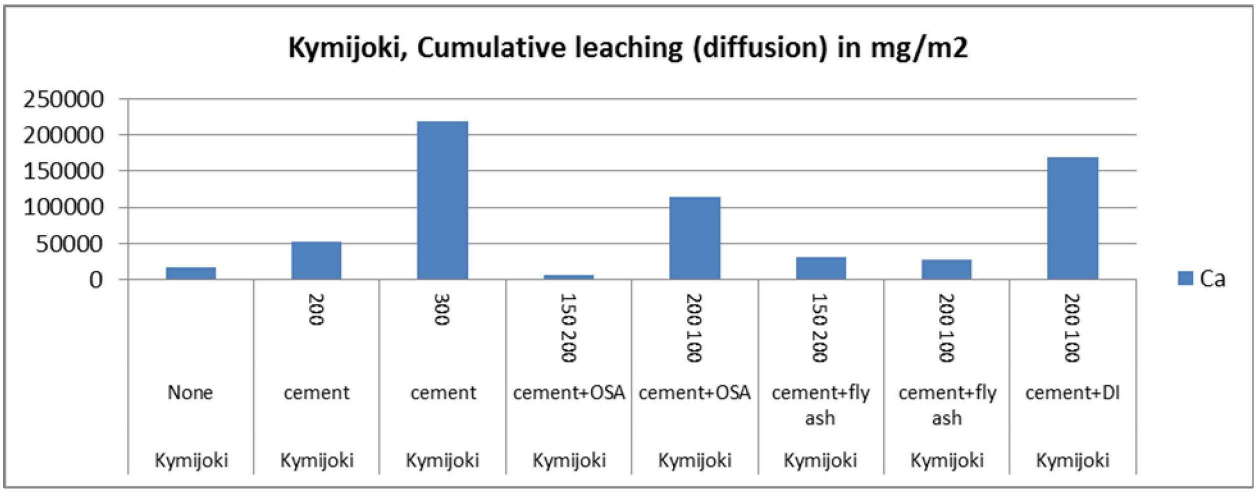

Figure 4.42 Cumulative leaching of calcium (original and stabilized samples). Sediment matrix is from river Kymijoki.

Excessive amounts of gypsum can be detected from increased values of diffused sulphate leaching, Figure 4.43.

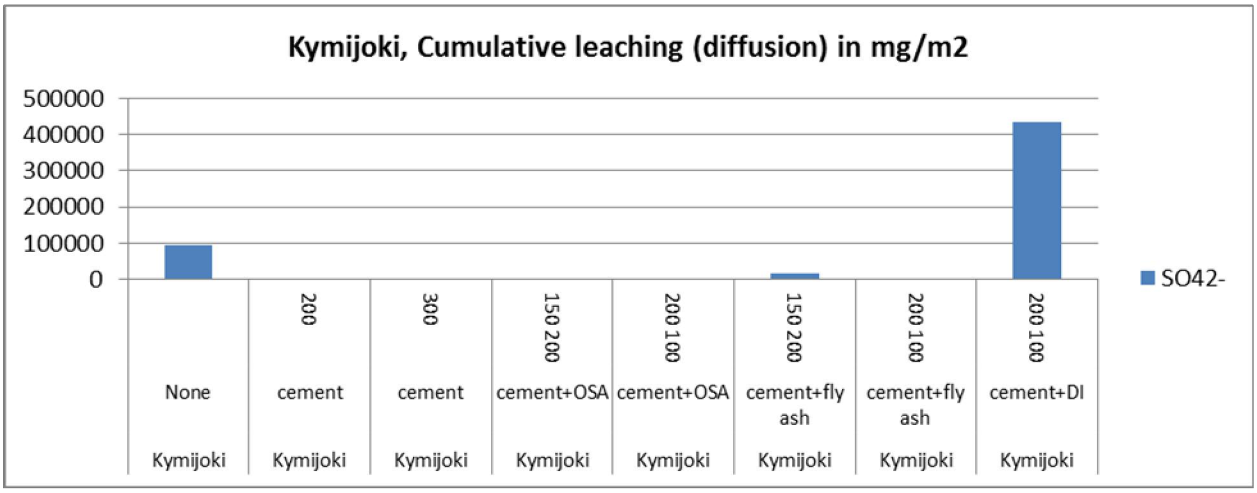

Figure 4.43 Cumulative leaching of sulphate (original and stabilized samples). Sediment matrix is from river Kymijoki.

4.6 SEM imaging

SEM imaging was used to compare differences in the stabilized structures. Test pieces made from Kymijoki matrix have all been stabilizing for the same period of time. In scanning electron microscopy, the sample is being showered with electrons with usually a voltage of 10 kV or 20 kV. These were also used in this case. The sample size needs to be reduced so that it fits in the equipment and dried. A prerequisite is that the sample has to be conductive. Since that is not the case with sediment samples, the samples were coated with a thin layer of gold.

In Figure 4.44 cement and fly ash have been selected as binder materials. In Figure 4.45 same amounts have been used but with oil shale ash. It has been found out that oil shale ash can provide a better result. By comparison of the Figures, it can be seen that the structure is more even and dense with oil shale ash than with fly ash. More crystalline structures have been formed with fly ash.

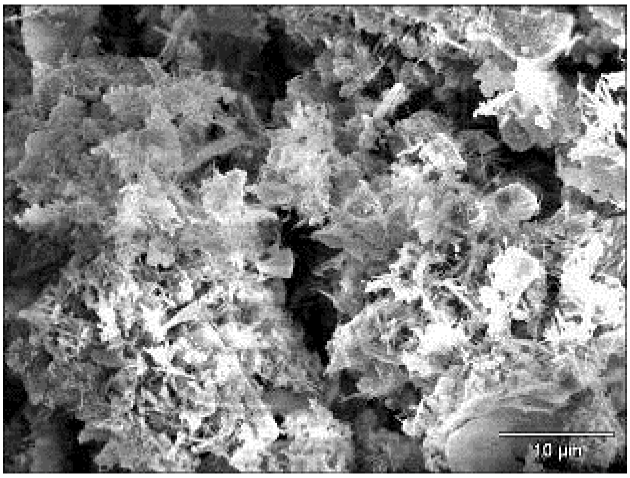

Figure 4.44 Cement and fly ash 100 + 200 kg/m^3 (Kymijoki)

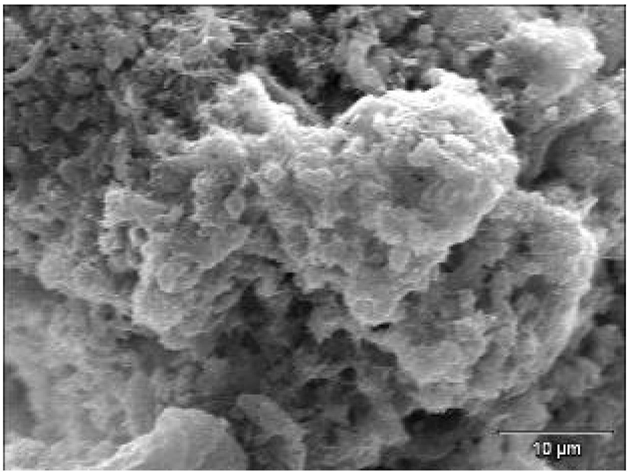

Figure 4.45 Cement and oil shale ash 100 + 200 kg/m^3 (Kymijoki)

By utilizing slag with cement, Figure 4.46, the structure can be seen to have high density and a large particle size distribution. Small long particles exist as well as larger crystalline structures. These together can form a dense and reasonably strong structure.

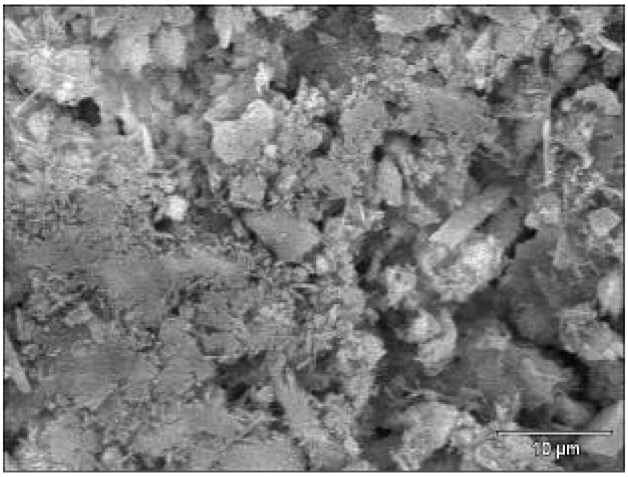

Figure 4.46 Cement and slag 100 + 200 kg/m^3 (Kymijoki)

In Figure 4.47, dihydrate gypsum has been used as a binder material with cement. The structure consists mainly of small long crystals but also with some larger crystals. This could well be found useful in long-term stabilization.

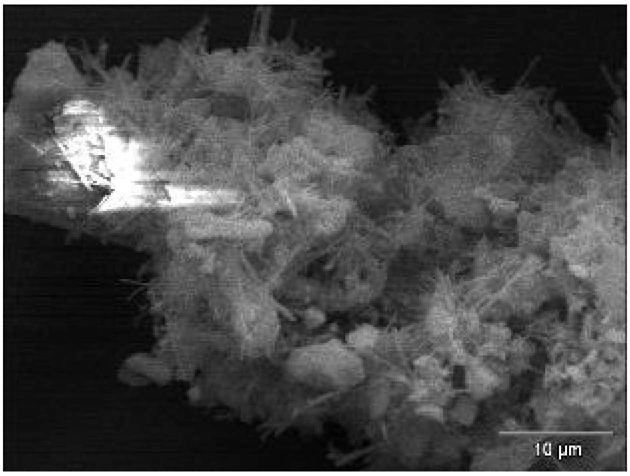

Figure 4.47 Cement and gypsum 100 + 200 kg/m^3 (Kymijoki)

In Figure 4.47, gypsum was used in natural state, but when this was compared to same amounts of binders using dried and pulverized gypsum, the structure can be seen to be highly different, Figure 4.48. Gypsum was dried for several days in 105 ºC in an oven and grinded thoroughly. The structure is denser visually and was found less brittle than sample in Figure 4.47. It seems that drying of the gypsum enhanced the reactivity significantly.

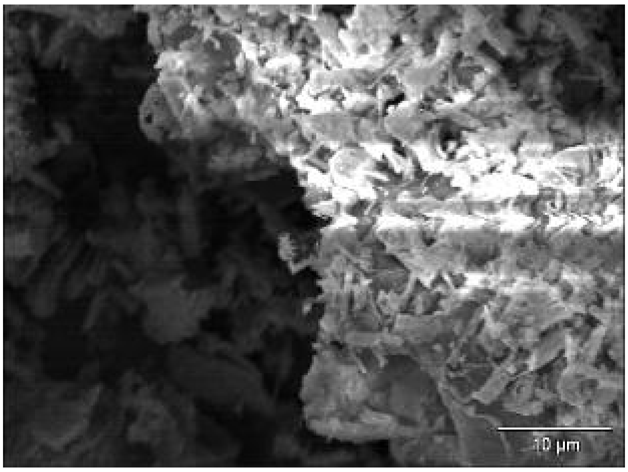

Figure 4.48 Cement and gypsum (dried and grinded) 100 + 200 kg/m^3 (Kymijoki)

When only fly ash was used, the structure, Figure 4.49, consists mainly of large crystals which are not tightly bound to each other. However, smaller grid-like structures between the crystals indicate an on-going reaction that would most probably provide long-term strength development.

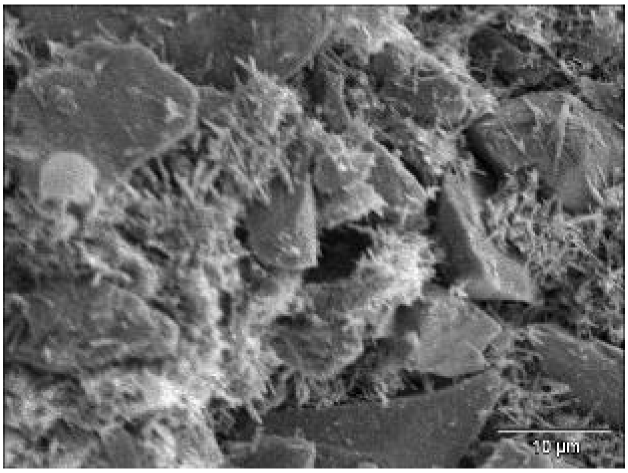

Figure 4.49 Fly ash 300 kg/m^3 (Kymijoki)

When oil shale ash was used, Figure 4.50, the structure is, in most areas, highly similar to that with fly ash. However, in some areas (Figure 4.51) the structure is very needle-like and well reacted.

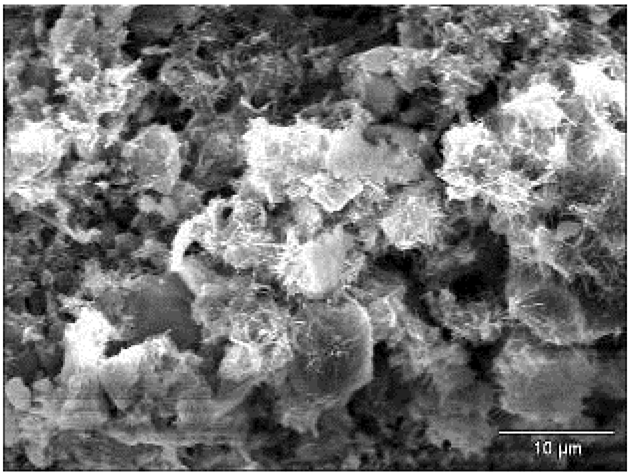

Figure 4.50 Oil shale ash 300 kg/m^3 (Kymijoki)

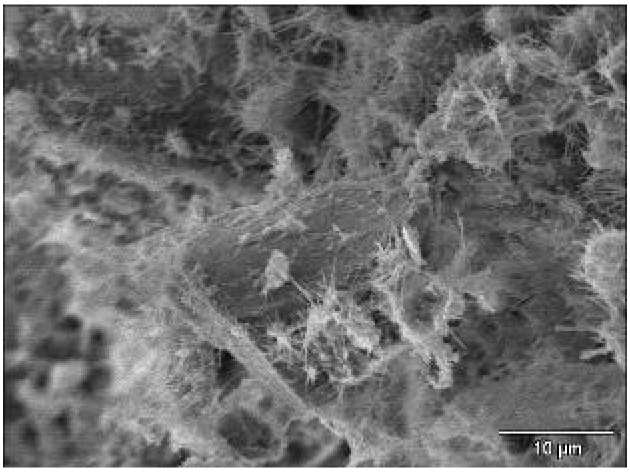

Figure 4.51 Oil shale ash 300 kg/m^3 (Kymijoki)

SEM pictures taken from samples that have been reacting for a year (matrix Port of Kokkola) show a long-term reaction results. Cement and oil shale ash were used as binder in sample in Figure 4.52. The structure consists of large crystals bound together with needle-like small crystals. Some very large particles have been formed, Figure 4.53.

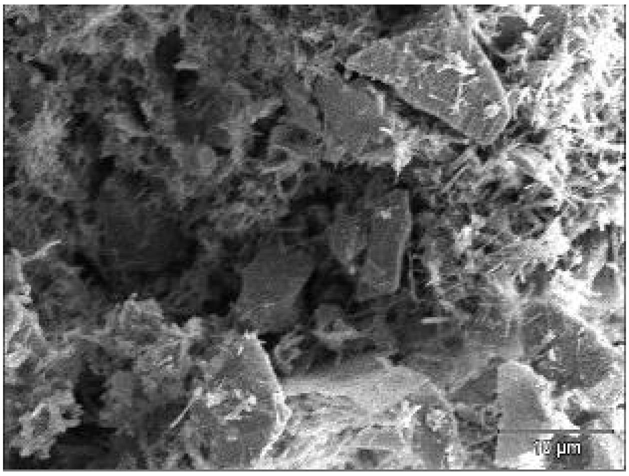

Figure 4.52 Cement and oil shale ash 40 + 150 kg/m^3 (Port of Kokkola)

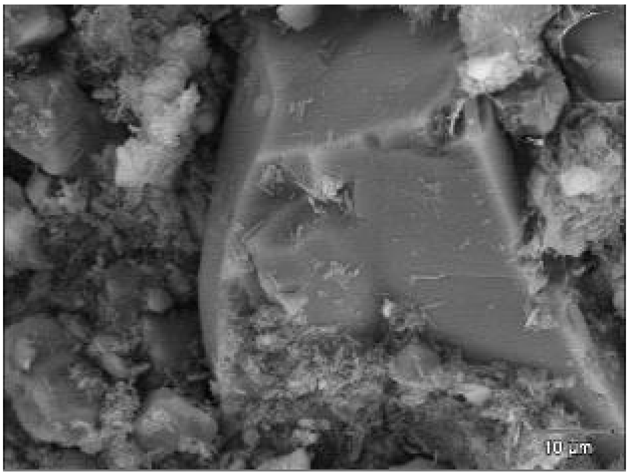

Figure 4.53 Cement and oil shale ash 40 + 150 kg/m^3 (Port of Kokkola)

In Figure 4.54, sample has been stabilized with only a small amount of cement. It can be seen that while some reactions have occurred, the structure is not very well bonded. This was found also during sample preparations as the sample was very brittle.

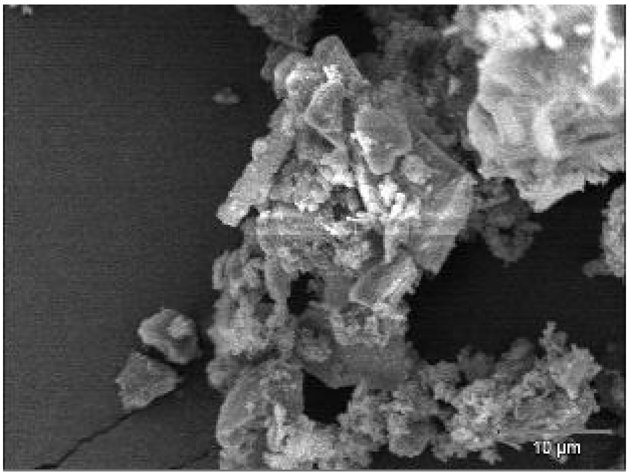

Figure 4.54 Cement 30 kg/m^3 (Port of Kokkola)

The structure is found more even by using fly ash as a binder, Figure 4.55. Particles are rather well bound together. While the reaction takes more time with only fly ash than with cement, better strength may result.

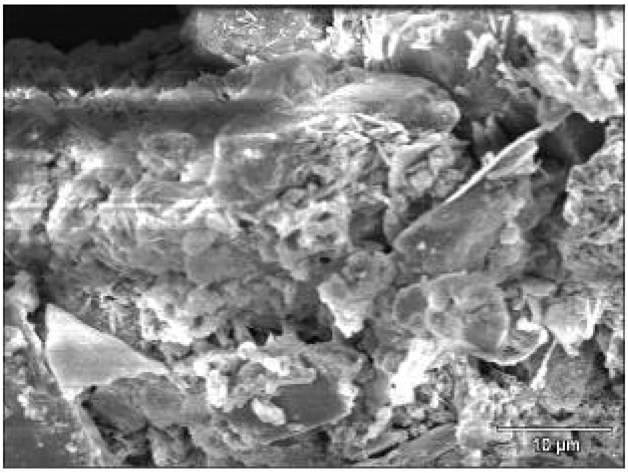

Figure 4.55 Fly ash 150 kg/m^3 (Port of Kokkola)

4.7 SEM imaging of binder materials

SEM imaging was done for dry binder materials. In Figure 4.56, cement is shown with magnification 2000.

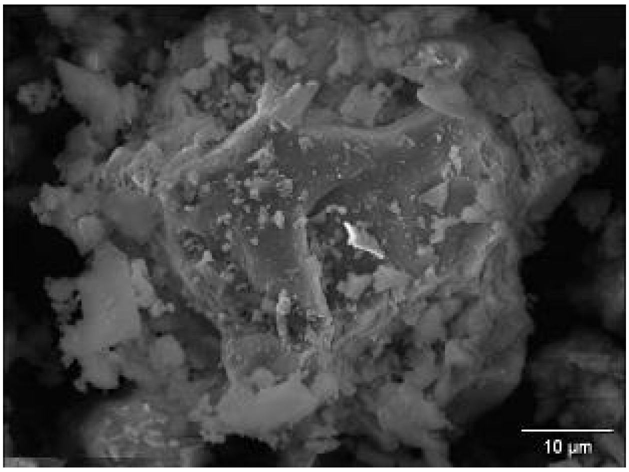

Figure 4.56   Cement sample

Ash structures often show spherical particles, as can be seen with fly ash in Figure 4.57 and 4.58.

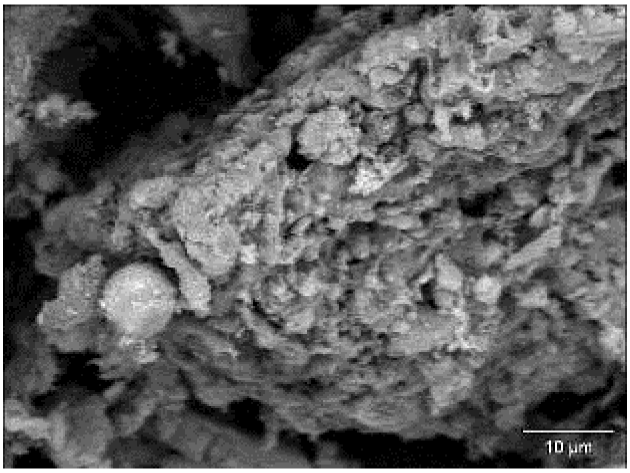

Figure 4.57   Fly ash

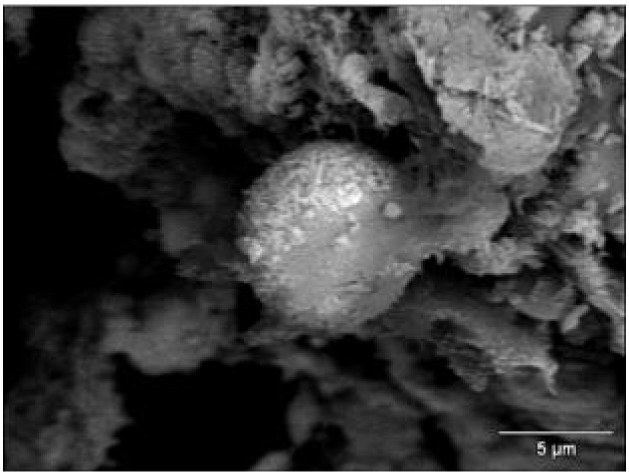

Figure 4.58   Fly ash. Magnification 5000.

Figure 4.59 shows typical surface of oil shale ash.

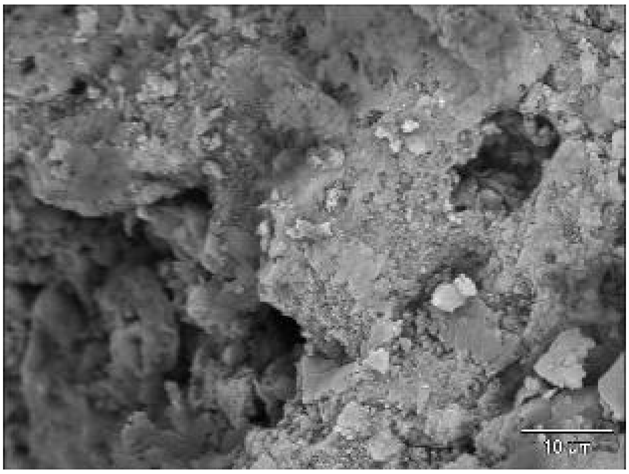

Figure 4.59   Oil shale ash sample

Typical structure of gypsum is shown in Figure 4.60.

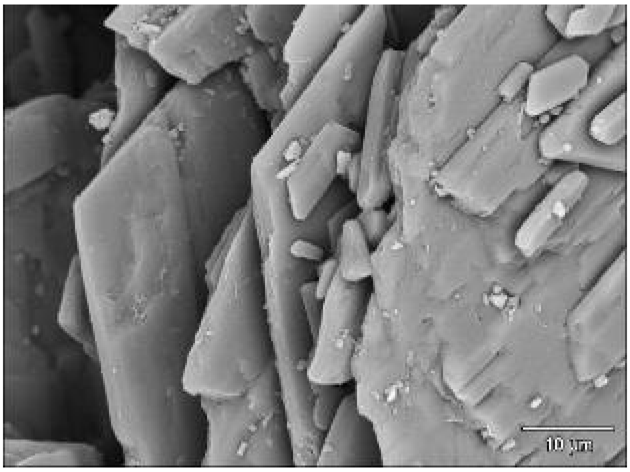

Figure 4.60 Gypsum sample

4.8 SEM imaging Kymijoki samples

Kymijoki sediment contains approximately 60 w-% water. The structure of dried material seems quite dense, Figure 4.61. However, the structure is very soft and contains a lot of organic material.

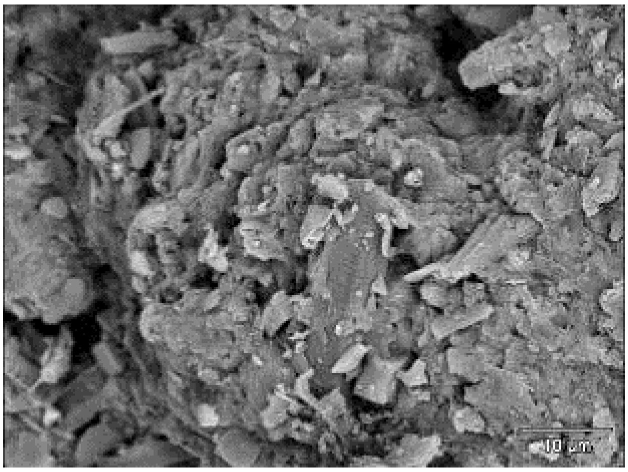

Figure 4.61 Unstabilized Kymijoki sample

Kymijoki sediment sample was stabilized using different binder materials and their mixtures. Figures 4.62 and 4.63 show structure with oil shale ash after one month curing period.

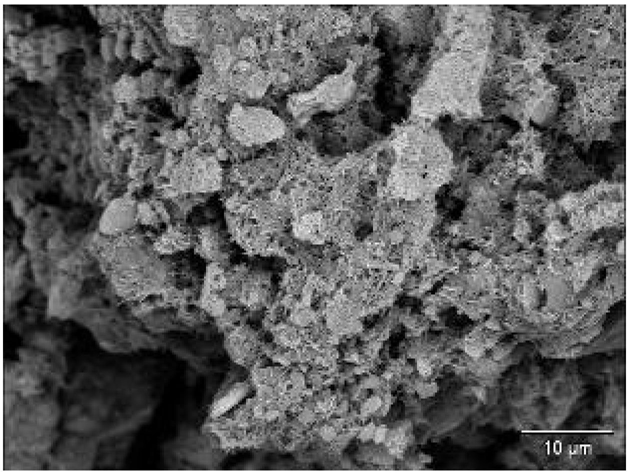

Figure 4.62 Kymijoki sample and oil shale ash 300 kg/m^3 after one month curing period.

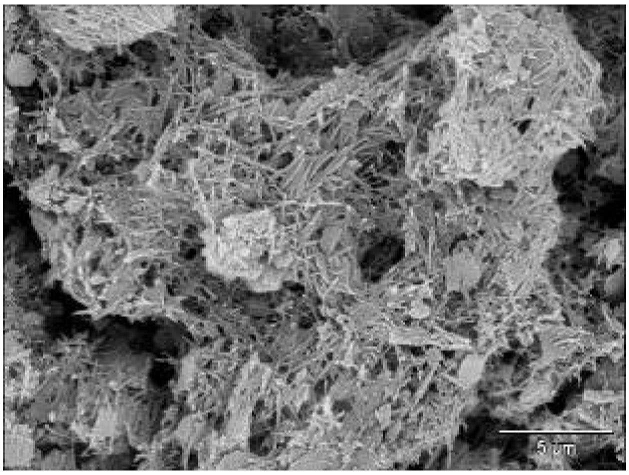

Figure 4.63 Kymijoki sample and oil shale ash 300 kg/m^3 after one month curing period (magnification 5000)

Figure 4.64 shows Kymijoki sample stabilized with fly ash 300 kg/m^3 after one month curing period.

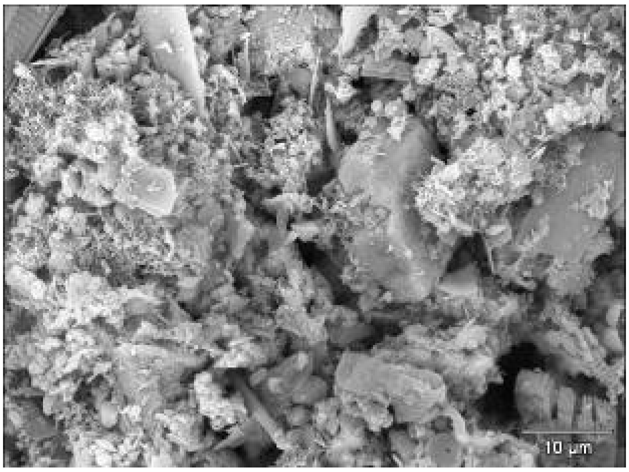

Figure 4.64 Kymijoki sample and fly ash 300 kg/m^3 after one month curing period

Mixture of cement and oil shale ash was used for stabilization. This is shown in Figures 4.65 and 4.66.

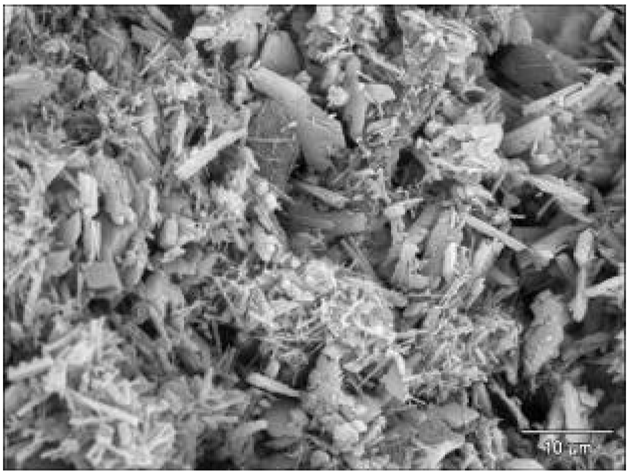

Figure 4.65 Kymijoki sediment stabilized with cement and oil shale ash mixture 100 + 200 kg/m^3.

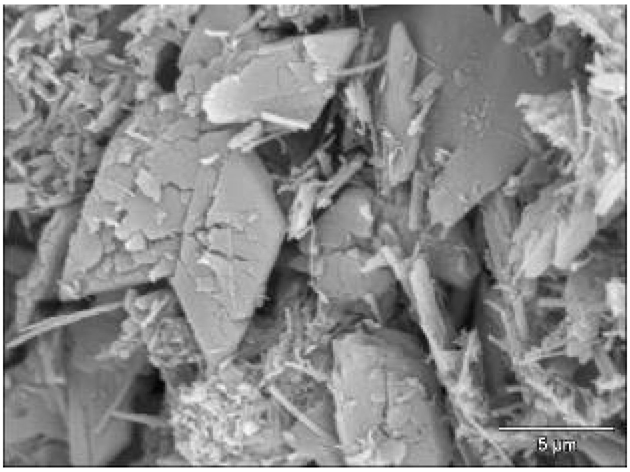

Figure 4.66 Kymijoki sediment stabilized with cement and oil shale ash mixture 100 + 200 kg/m^3.

Figures 4.67 and 4.68 show Kymijoki sediment stabilized with a mixture of cement and gypsum (100 + 200 kg/m^3) after one month curing period. Gypsum was dried before use.

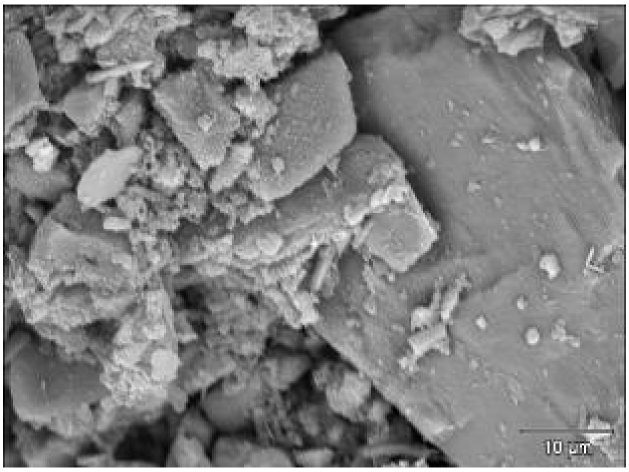

Figure 4.67 Kymijoki sediment stabilized with a mixture of cement and gypsum (100 + 200 kg/m^3) after one month curing period. Gypsum was dried before use.

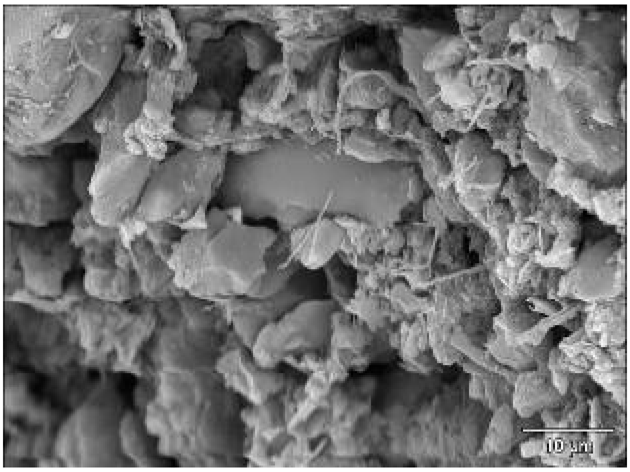

Figure 4.68 Kymijoki sediment stabilized with a mixture of cement and gypsum (100 + 200 kg/m^3) after one month curing period. Gypsum was dried before use.

Kymijoki sample was stabilized with oil shale ash (150 kg/m^3). The structure after 4 days can be seen in Figures 4.69 and 4.70.

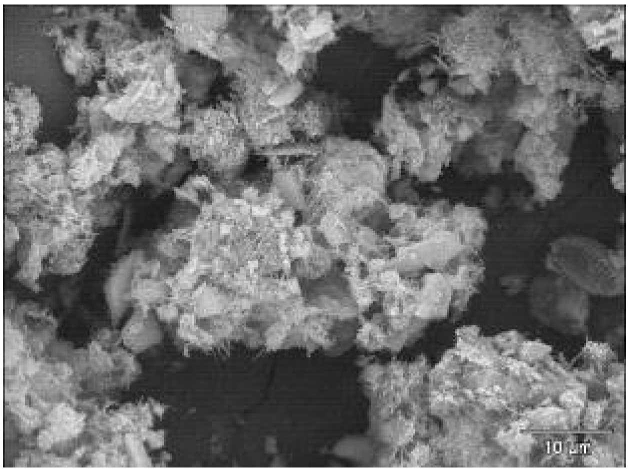

Figure 4.69 Kymijoki sediment stabilized with oil shale ash 150 kg/m^3 after 4 days curing period.

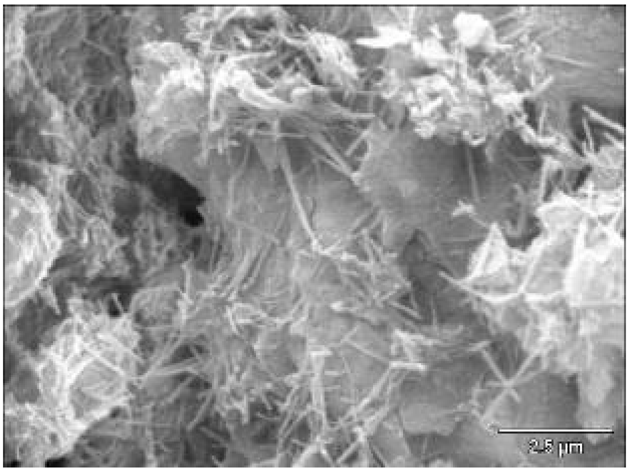

Figure 4.70 Kymijoki sediment stabilized with oil shale ash 150 kg/m^3 after 4 days curing period. Magnification 10000.

4.9 SEM imaging Kokkola samples

The sediment sample from Port of Kokkola was imaged before stabilization, Figures 4.71 and 4.72. It can be seen that the structure has a large particle size distribution.

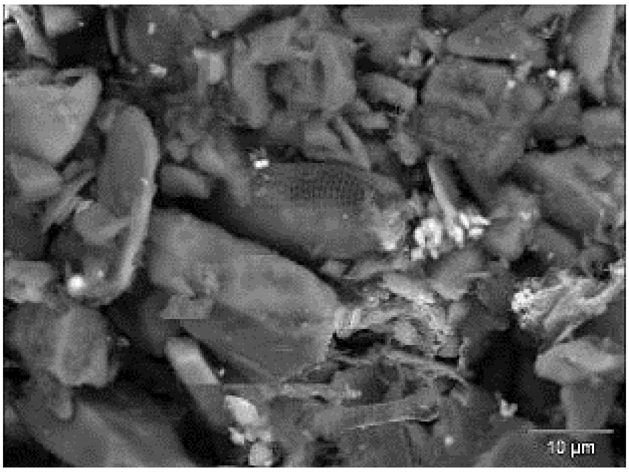

Figure 4.71 Unstabilized Kokkola sample

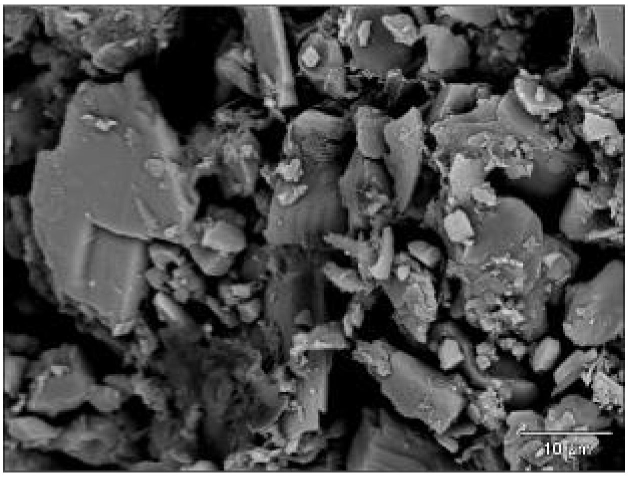

Figure 4.72 Unstabilized Kokkola sample

Kokkola sediment sample was stabilized using different binder materials and their mixtures. Figure 4.73 shows sample stabilized with oil shale ash and after one month curing period.

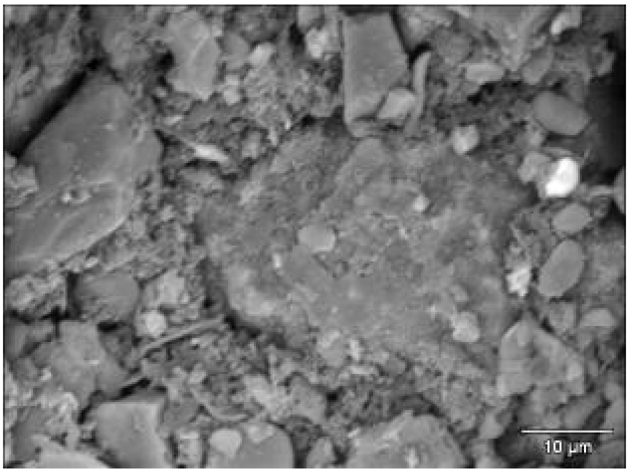

Figure 4.73 Kokkola sample and oil shale ash 200 kg/m^3 after one month curing period.

Figures 4.74 and 4.75 show Kokkola sample stabilized with cement 70 kg/m^3 after one month curing period. Cement reactions have yielded into large silicate crystals.

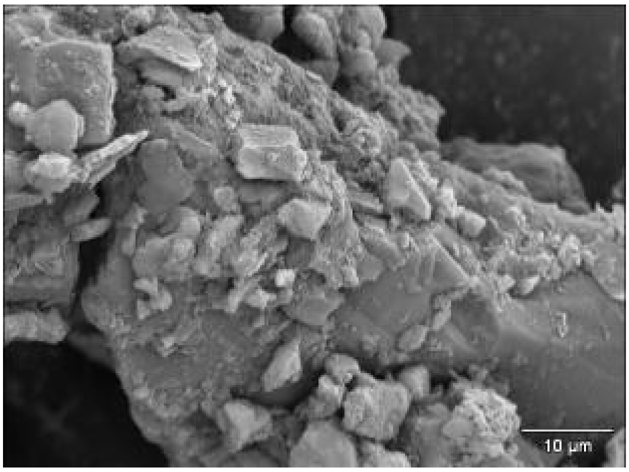

Figure 4.74 Port of Kokkola sediment sample stabilized with cement 70 kg/m^3 after one month curing period.

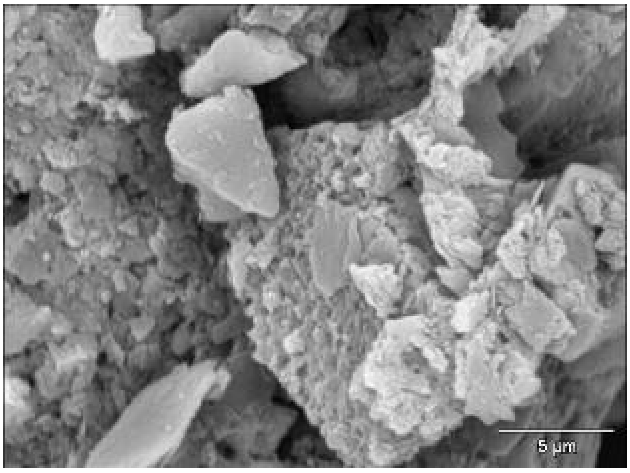

Figure 4.75 Port of Kokkola sediment sample stabilized with cement 70 kg/m^3 after one month curing period. Magnification 5000.

4.10 SEM imaging Gävle samples

Figure 4.76 shows Gävle sediment stabilized with cement and gypsum (50+25 kg/m^3) after one month curing period.

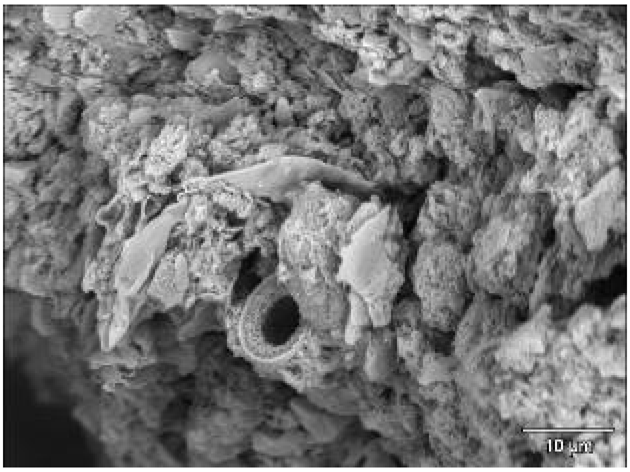

Figure 4.76 Gävle sediment sample stabilized with cement and gypsum after one month curing period.

Figure 4.77 shows Gävle sediment stabilized with cement and oil shale ash (50+50 kg/m^3) after one month curing period.

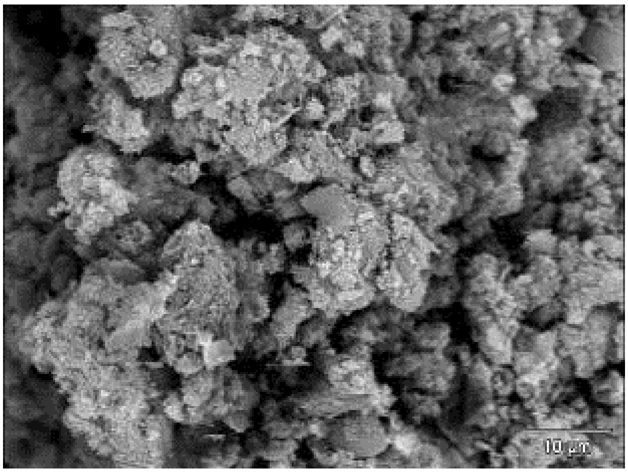

Figure 4.77 Gävle sediment sample stabilized with cement and oil shale ash (50+50 kg/m^3) after one month curing period.

Figures 4.78 and 4.79 show Gävle sediment stabilized with cement and fly ash (50+50 kg/m^3) after one month curing period.

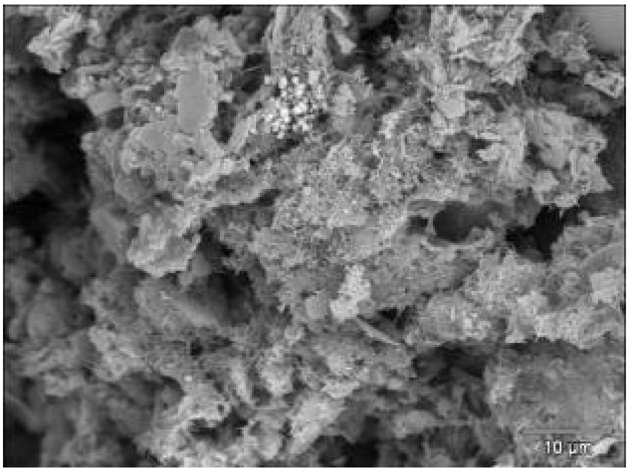

Figure 4.78 Gävle sediment sample stabilized with cement and fly ash (50+50 kg/m^3) after one month curing period.

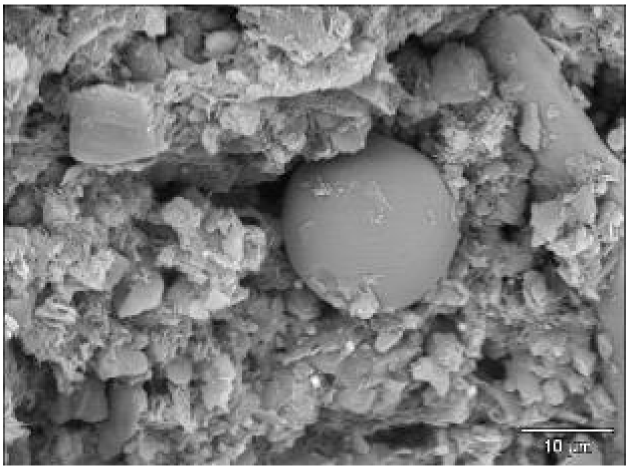

Figure 4.79 Gävle sediment sample stabilized with cement and fly ash (50+50 kg/m^3) after one month curing period.

4.11 SEM imaging of sample curing

SEM images were taken from samples that were stabilized different times. The samples are done on Kokkola matrix using cement 100 kg/m^3 as the binder material. Figure 4.80 shows the structure after 4 days curing period in 35 °C temperature. It can be seen that small needle-like crystals have been formed but the structure lacks larger calcium silicate hydrate structures.

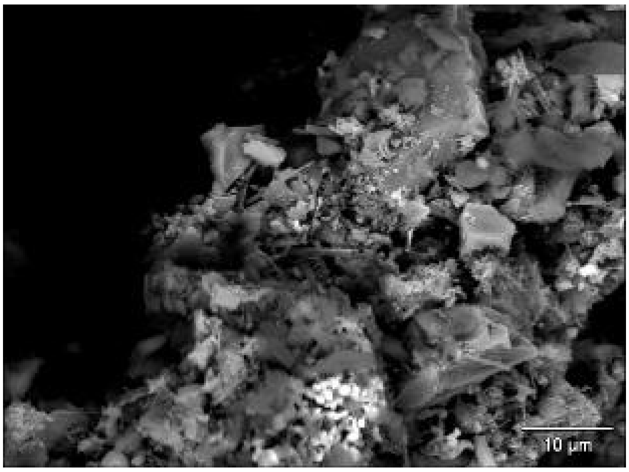

Figure 4.80 Sample Kokkola, binder cement 100 kg/m^3 after 4 days in 35 °C.

After 7 days, more needle-like crystals can be seen and they are starting to form spherical structures and to bind larger crystals into a grid, Figure 4.81.

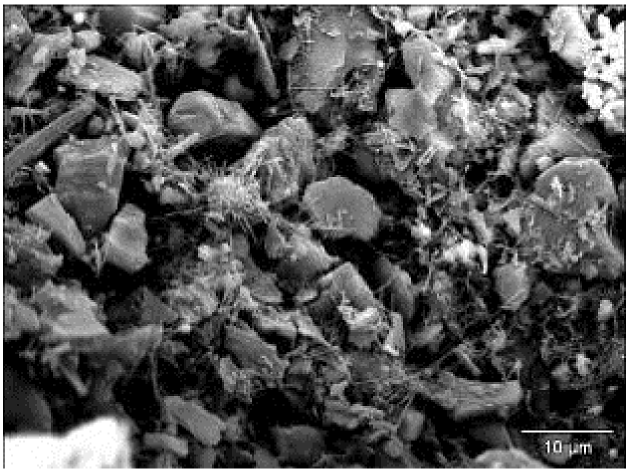

Figure 4.81 Sample Kokkola, binder cement 100 kg/m^3 after 7 days in 35 °C.

After 14 days, clearly more large crystals have been formed. Less of the needle-like crystals are shown, Figure 4.82.

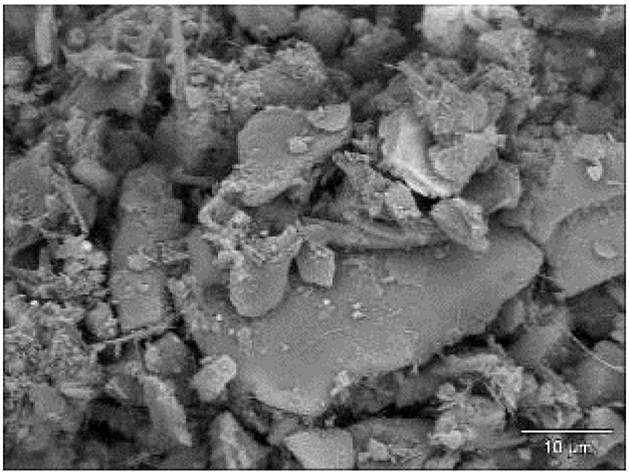

Figure 4.82 Sample Kokkola, binder cement 100 kg/m^3 after 14 days in 35 °C.

In room temperature ~20 °C, sample has been reacting slower. In Figure 4.70 (room temperature) it can be seen that compared to Figure 4.83, less of the large crystals are formed and more of the needle-like crystals are present.

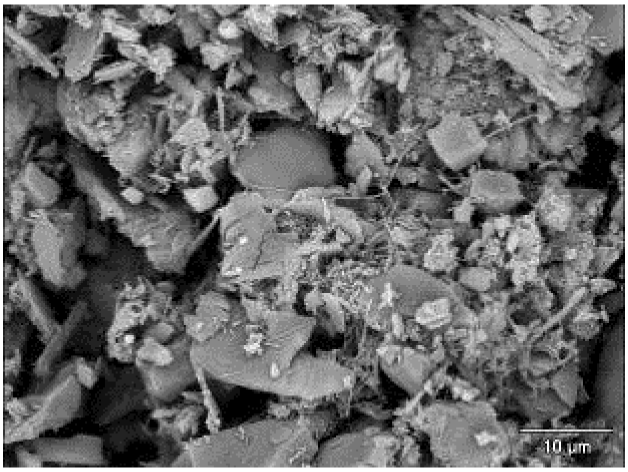

Figure 4.83 Sample Kokkola, binder cement 100 kg/m^3 in room temperature after 14 days.

After 28 days the sample seems well reacted, Figure 4.84. It can be seen that very large crystals have been formed and dense sponge-like calcium silicate hydrate is filling the space between crystals.

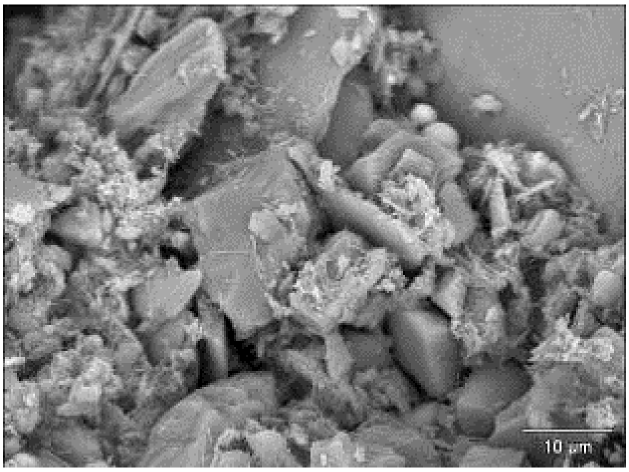

Figure 4.84 Sample Kokkola, binder cement 100 kg/m^3 in room temperature after 28 days.

4.12 Statistical effect of binder materials on element leaching

Different binder materials effect on leaching of elements was examined using the data from the experimental design. Two models were formed for each element (or compound); one for Port of Kokkola sediment and another for Kymijoki river sediment. Coefficients for binder materials are shown for elemets (or compounds) that have statistical significance. These results are case sensitive and should only be used for comparative purposes between binder materials and sediment.

Leaching of calcium is shown in Figure 4.85. Both models have statistical significance. The addition of gypsum adds the leaching of calcium in both cases. In Kokkola case, it seems that the addition of oil shale ash was the most effective in reducing leaching, i.e. calcium has been effectively used in the cement reaction to form stable calcium silicate hydroxide gel. Slag seems to be most effective in case Kymi.

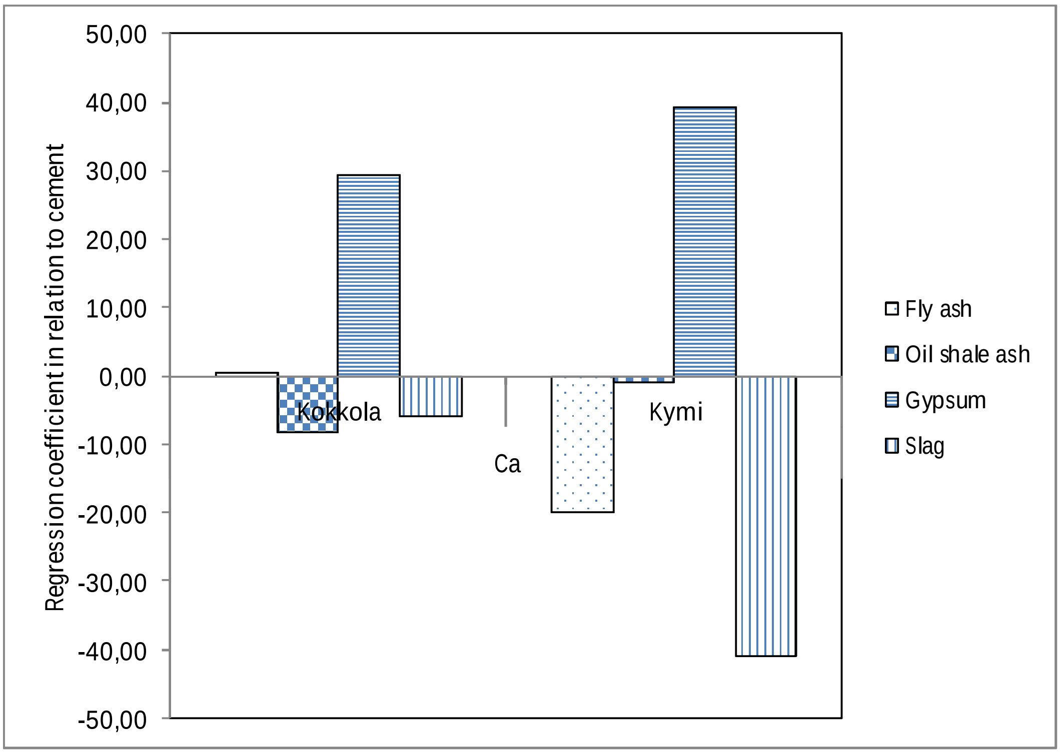

Figure 4.85 The effect of binder materials on the leaching of calcium

As expected, the addition of gypsum leads to leaching of sulphate, Figure 4.86.

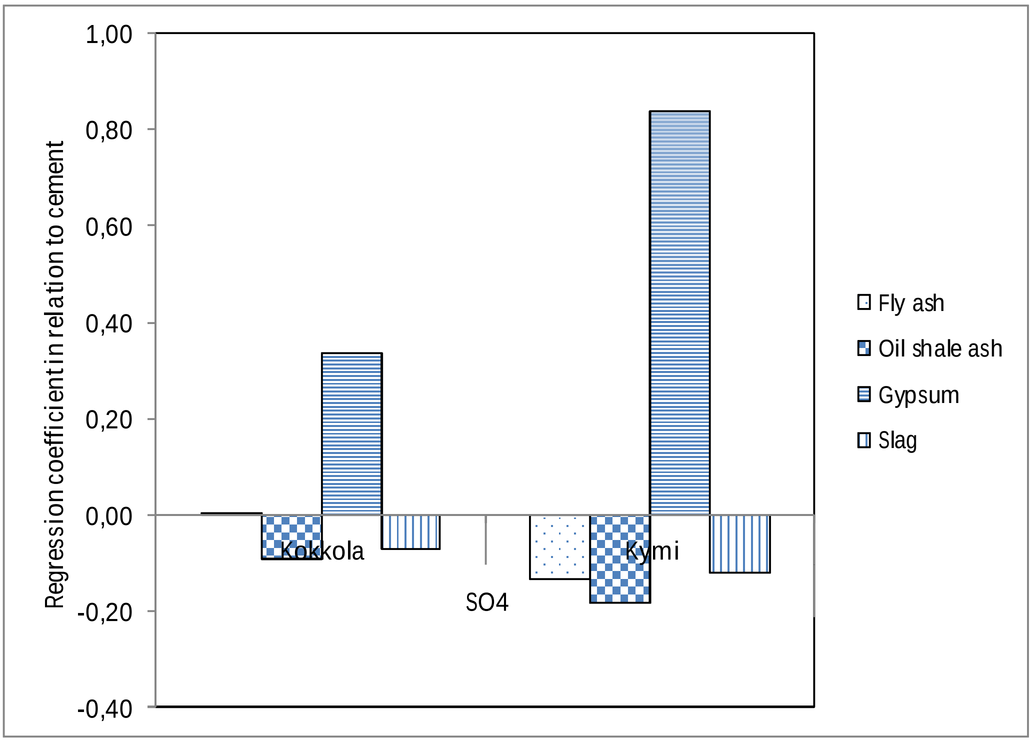

Figure 4.86 The effect of binder materials on the leaching of sulphate

Leaching of copper can be reduced most efficiently using slag in both studied cases. In case Kymi, it seems that adding fly ash has not been as effective on binding Cu as oil shale ash. However, the situation is reversed in case Kokkola, while neither seems to have a special advantage. Gypsum has reduced the leaching in both cases, Figure 4.87.

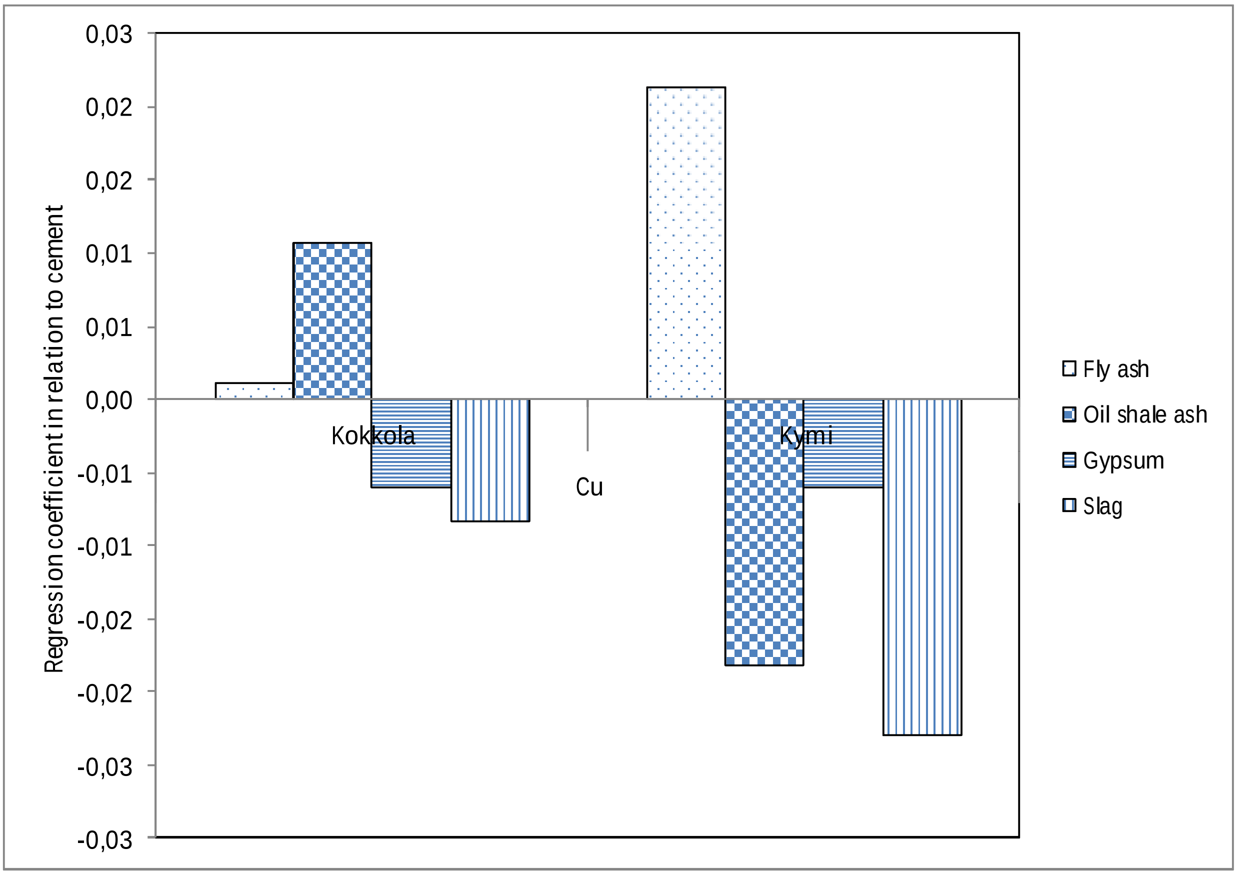

Figure 4.87 The effect of binder materials on the leaching of copper

For reducing leaching of magnesium, it seems that oil shale ash is the most effective in case Kymi, while in case Kokkola slag has been the most effective. This is shown in Figure 4.88.

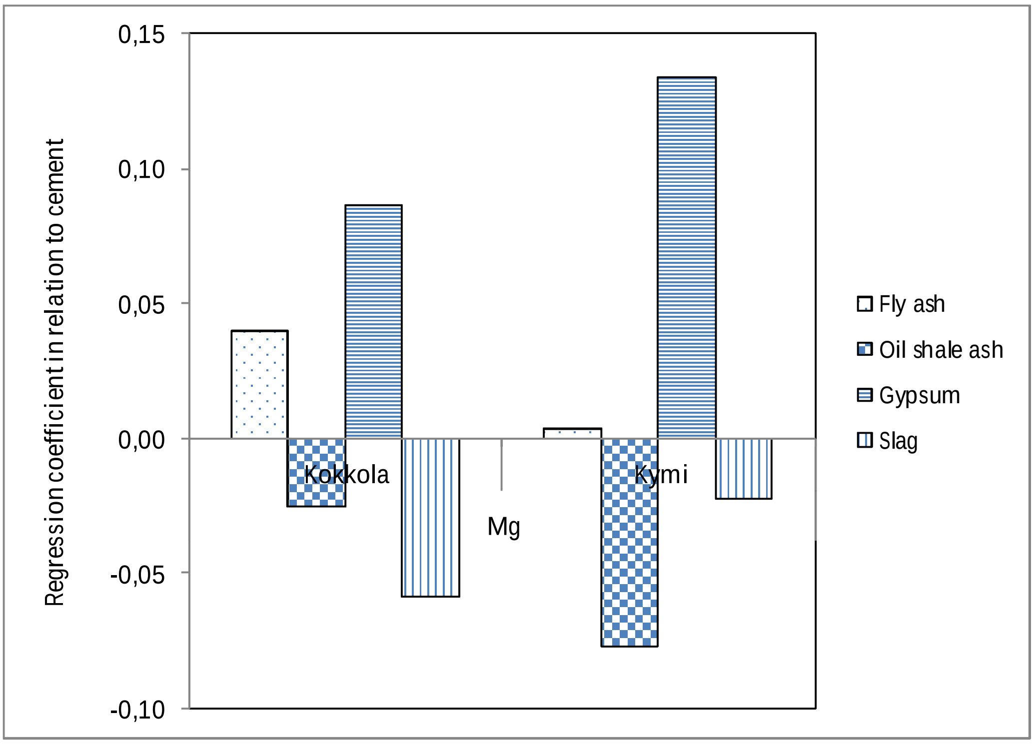

Figure 4.88 The effect of binder materials on the leaching of copper

Leaching of nickel is suspected to be caused by the addition of cement. Most efficiently this can be reduced by addition of slag in case Kymijoki and by addition of fly ash in case Kokkola, Figure 4.89.

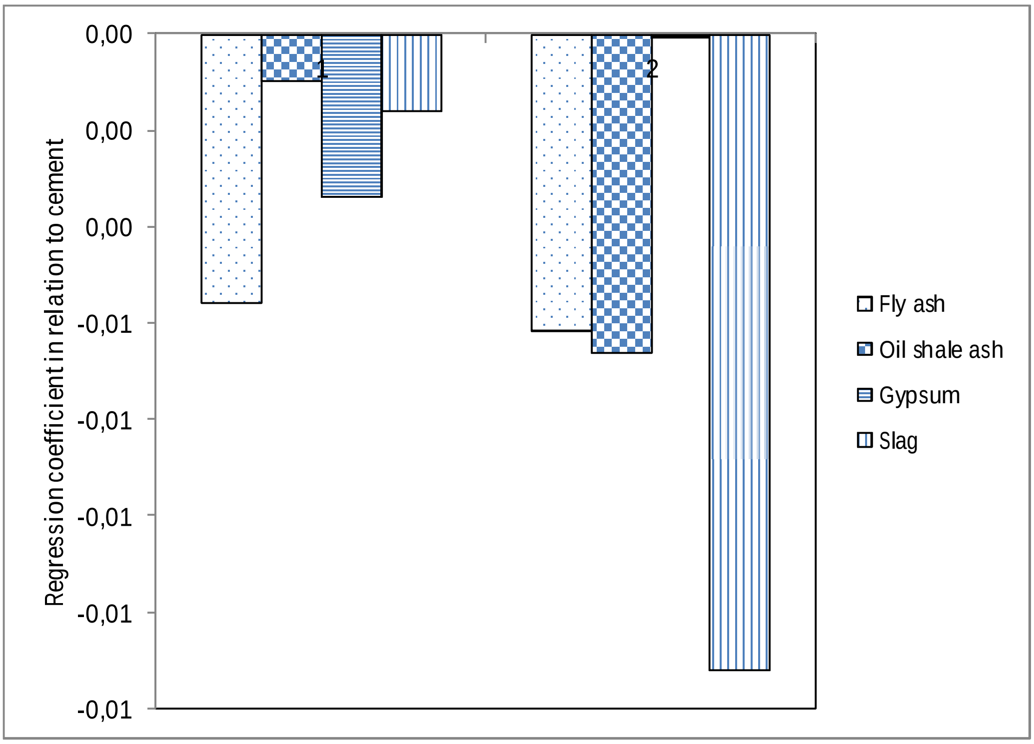

Figure 4.89 The effect of binder materials on the leaching of nickel

Leaching of chloride can be reduced by addition of gypsum in case Kokkola, Figure 4.90. Slag seems effective in case Kymi, but that should be discarded seeing that the model is not statistically significant (59.0 %).

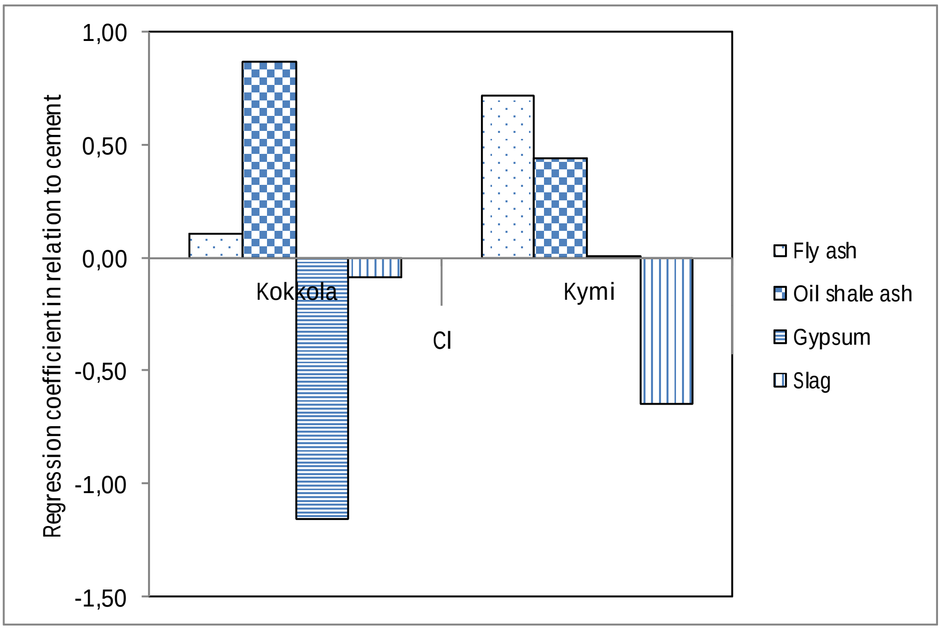

Figure 4.90 The effect of binder materials on the leaching of chloride

Leaching of iron can be reduced efficiently with adding of fly ash or oil shale ash, Figure 4.91. However, both models have relative low significances (Kokkola 80.3 % and Kymi 66.4 %).

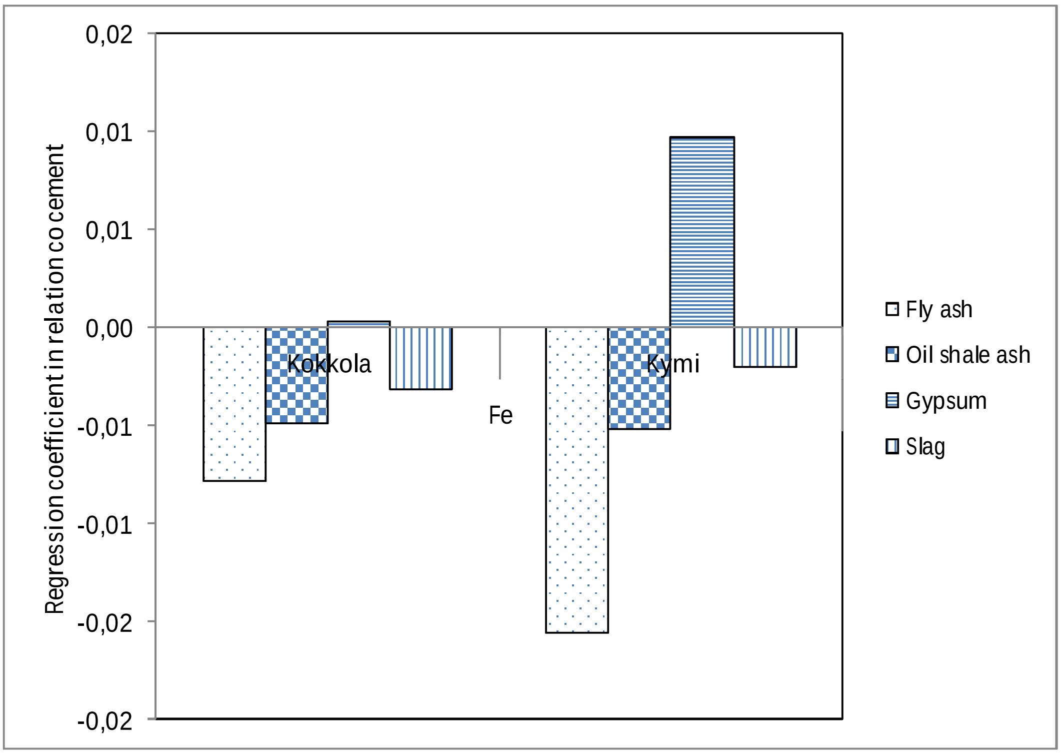

Figure 4.91 The effect of binder materials on the leaching of iron

For reducing the leaching of zinc, which was found the main problem in case Kokkola, in both cases the concentrations from stabilized structures were low, barely above detection limit. The reduction of leaching was near 100 % with all considered binders with cement. Due to this, model for case Kokkola has statistical significance 26.4 %. Model for case Kymi has some statistical significance (91.8 %), but the concentrations are still very low. A conclusion could still be made that ashes, fly ash and oil shale ash, have a positive effect on stabilization, Figure 4.92.

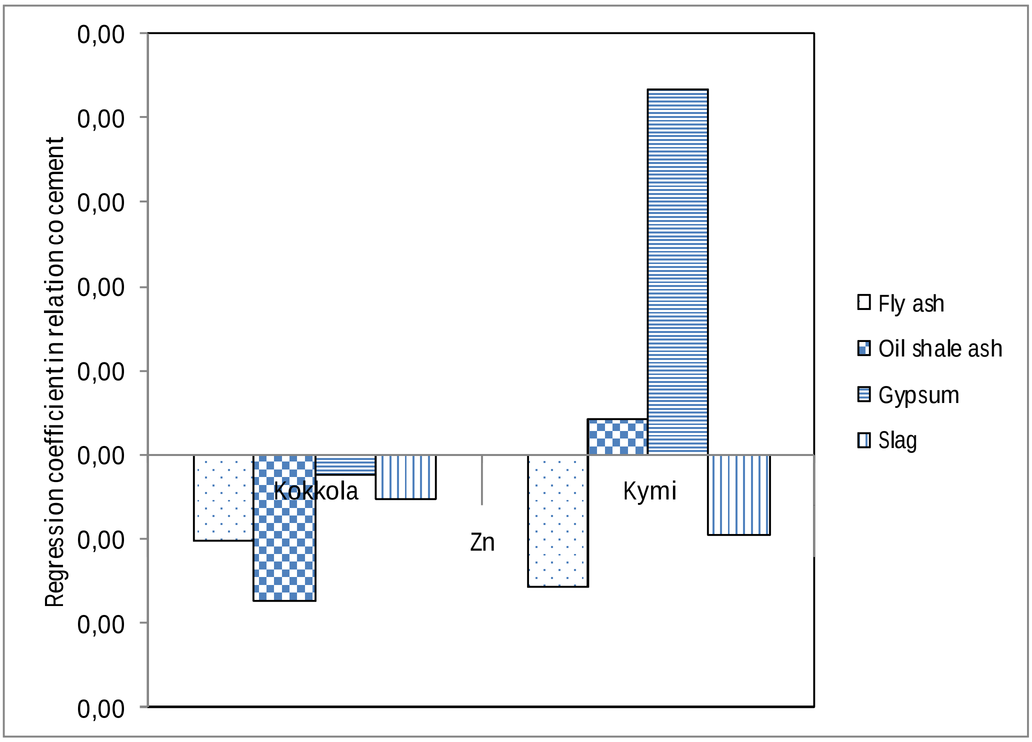

Figure 4.92 The effect of binder materials on the leaching of zinc

4.13 Effect of stabilization conditions

Heat treatment can be used in order to obtain a notion of stabilized strength faster. A common approach is to cure samples in a refrigerator for a period of 28 days. Sometimes the knowledge is needed earlier and then heat treatment in 35 °C can be used.

The effect of heat treatment was investigated by curing parallel samples in either room temperature 20 °C or °C or 35 °C for a period of 4, 7, 14, and 28 days. The effectiveness of stabilization was evaluated by batch testing and measuring several elements from leachates. Different elements and compounds are shown in Figures 4.93 – 4.97.

It can be seen that after 14 days of stabilization, the heat treated samples have higher leaching than those in room temperature. It indicates that the reaction has advanced further due to heat treatment and the increasing trend in leaching can be expected. It is to be expected that the cumulative leaching will continue to increase even after 28 days.

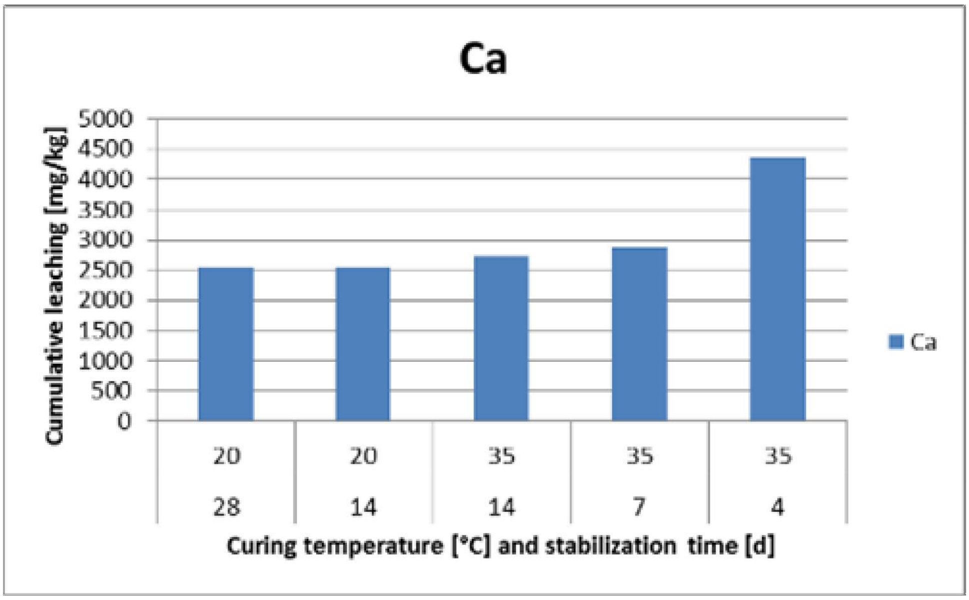

Figure 4.93 Leaching of Ca from stabilized samples after 4, 7, 14, and 28 days in 20 °C or 35 °C.

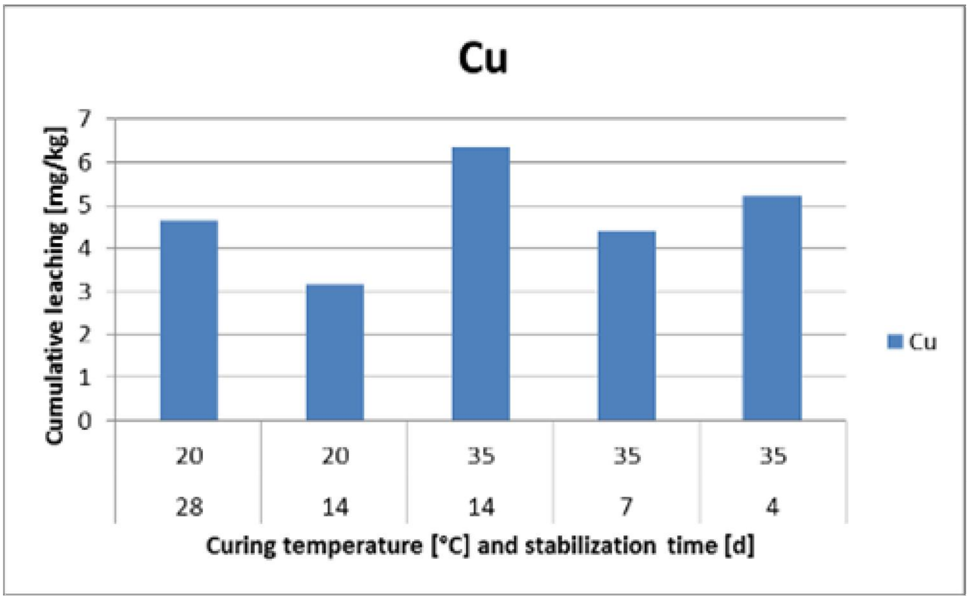

Figure 4.94 Leaching of Cu from stabilized samples after 4, 7, 14, and 28 days in 20 °C or 35 °C.

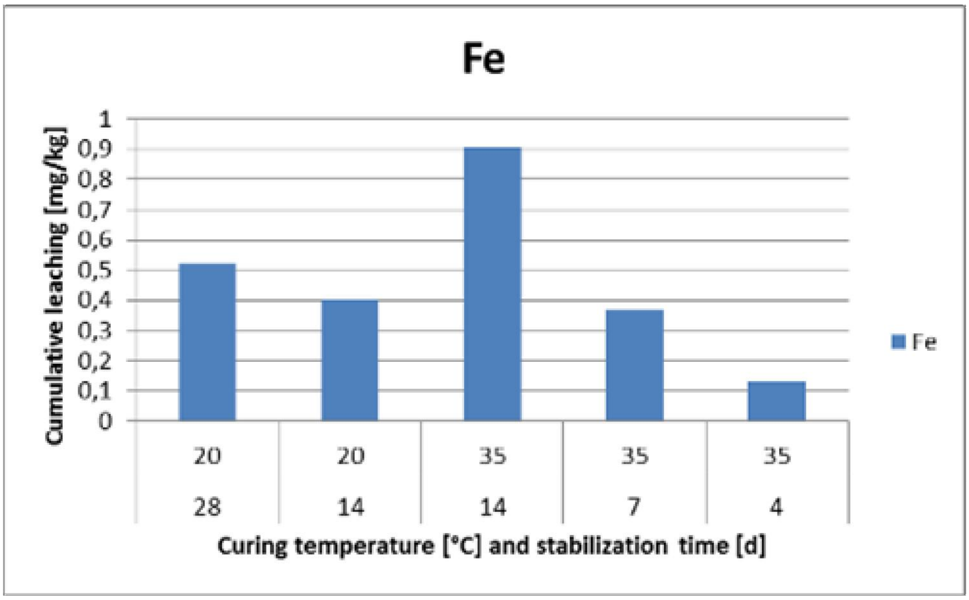

Figure 4.95 Leaching of Fe from stabilized samples after 4, 7, 14, and 28 days in 20 °C or 35 °C.

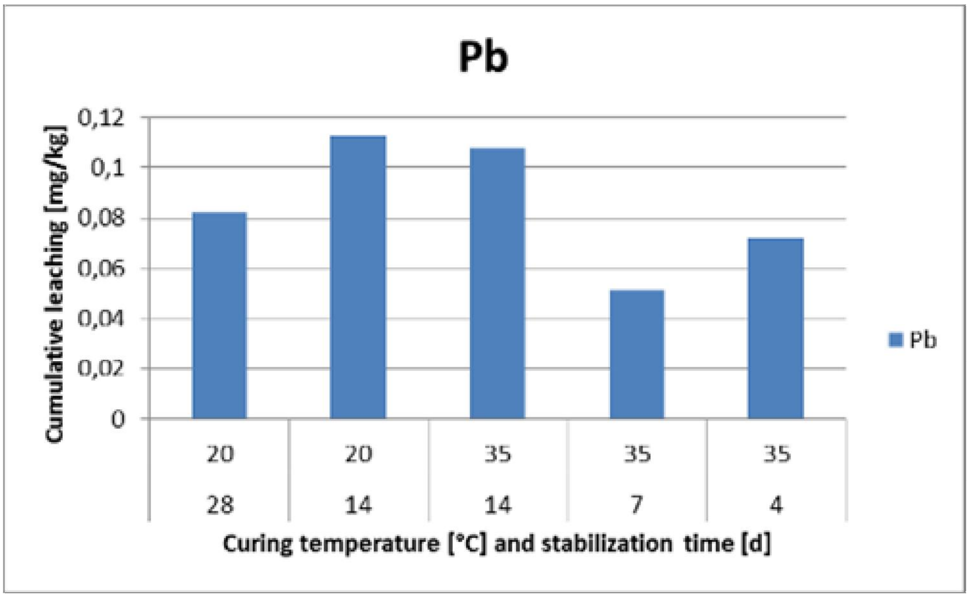

Figure 4.96 Leaching of Pb from stabilized samples after 4, 7, 14, and 28 days in 20 °C or 35 °C.

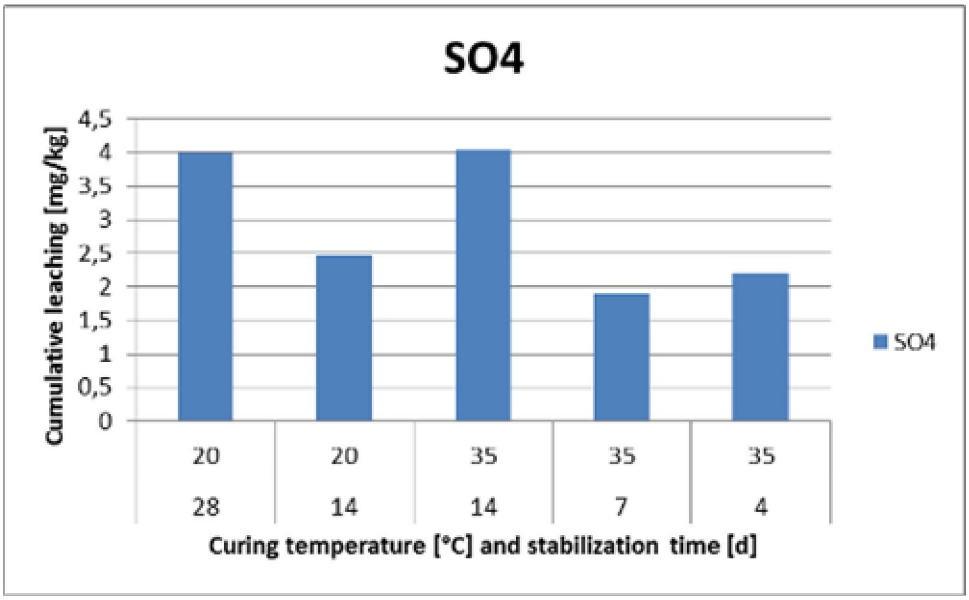

Figure 4.97 Leaching of SO_4^{2-} from stabilized samples after 4, 7, 14, and 28 days in 20 °C or 35 °C.

4.14 Heterogeneity of stabilized test pieces

The following samples from Port of Kokkola sediment, Table 4.4, were tested by dividing the sample into two and analyzing the halves separately with a single-stage batch test.

Table 4.4 Tested samples for heterogeneity of stabilization

	[kg/m3]				
	Fly ash	Oil shale ash	gypsum	Slag	Cement
1					50
2					50
3	200				
4			200		50
5		150			40
6	150				40
7	100		100		40
8		150	100		30

The results of this are shown in Figure 4.98 as an average difference of the cumulative leaching value from the mean value. A few characteristic elements or compounds are shown.

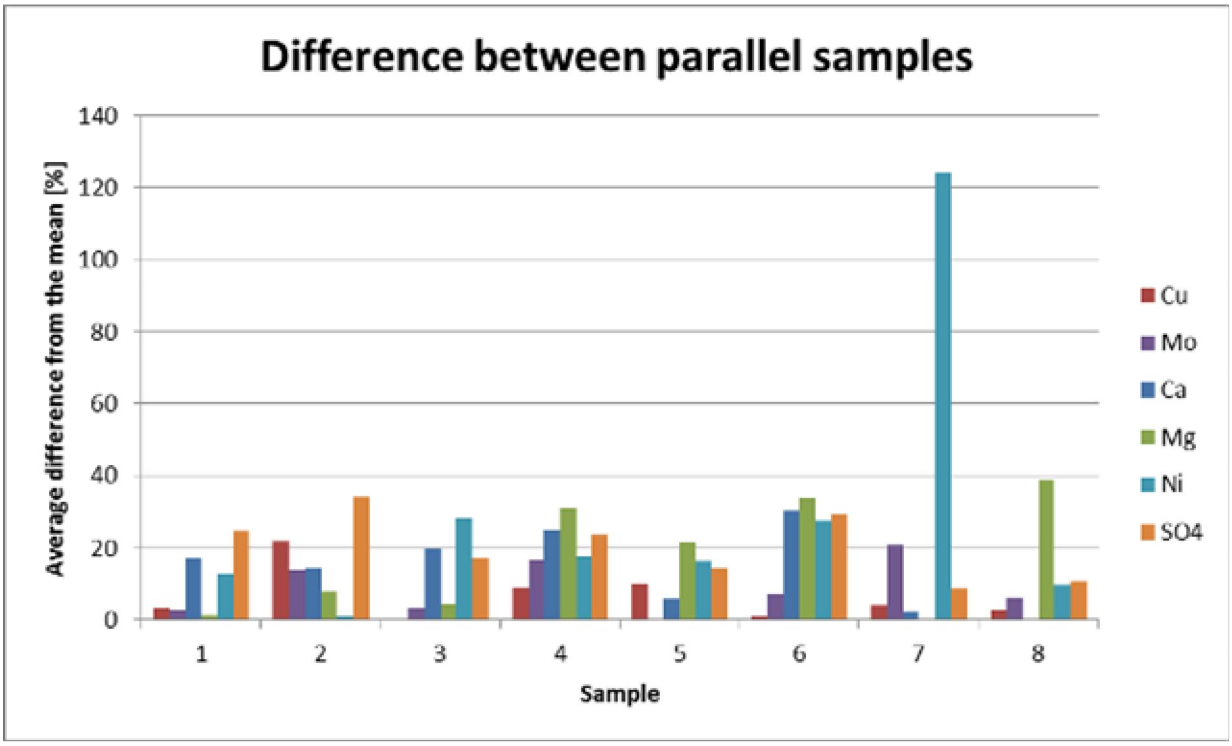

Figure 4.98 Heterogeneity of stabilization samples

4.15 Leaching order during batch testing

The cumulative two stage batch test is done in a way that the sample is shaken for 6 hours with L/S ratio 2 and 18 hours with L/S ratio 8. The effectiveness of the method and dynamics of the stabilization process was evaluated with a modified approach to batch testing. All the samples had the same sediment matrix, i.e., Port of Kokkola. For stabilization a few different compositions of binder materials were selected.

In the modified approach, a sample of leachate was collected at several time steps. The first sample was taken after one hour agitation. The last sample was taken after 48 hours. At each step, the extracted volume of liquid was replaced with the same amount to maintain constant L/S ratio. The cumulative results were calculated with a modified approach to the standard. The results are shown in Figures 4.99-4.108.

The leaching concentrations are low, but it can be seen from, e.g., calcium that the level sets at a constant after 24 hours indicating that main pozzolanic reactions have occurred and cumulative calcium level has reached an equilibrium. Different elements seem to have highly different trends, either increasing or decreasing. With zinc the beginning of testing gives very different results depending on the binder material. However, it seems that after a while the differences will diminish and the binding of zinc in stabilized material continues.

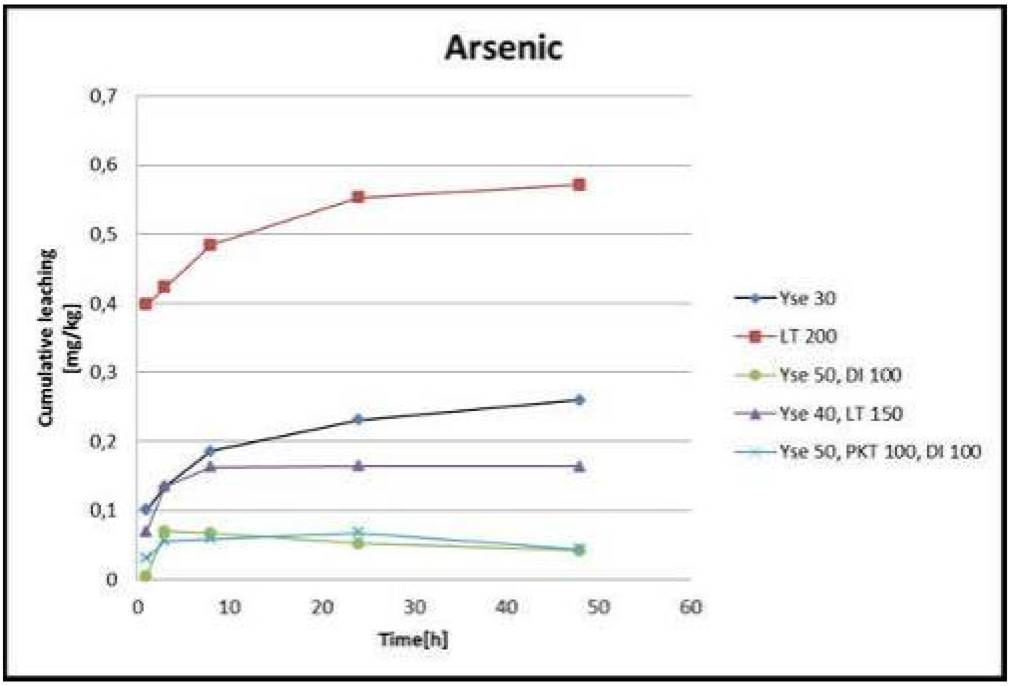

Figure 4.99 Arsenic leaching from stabilized material during batch testing

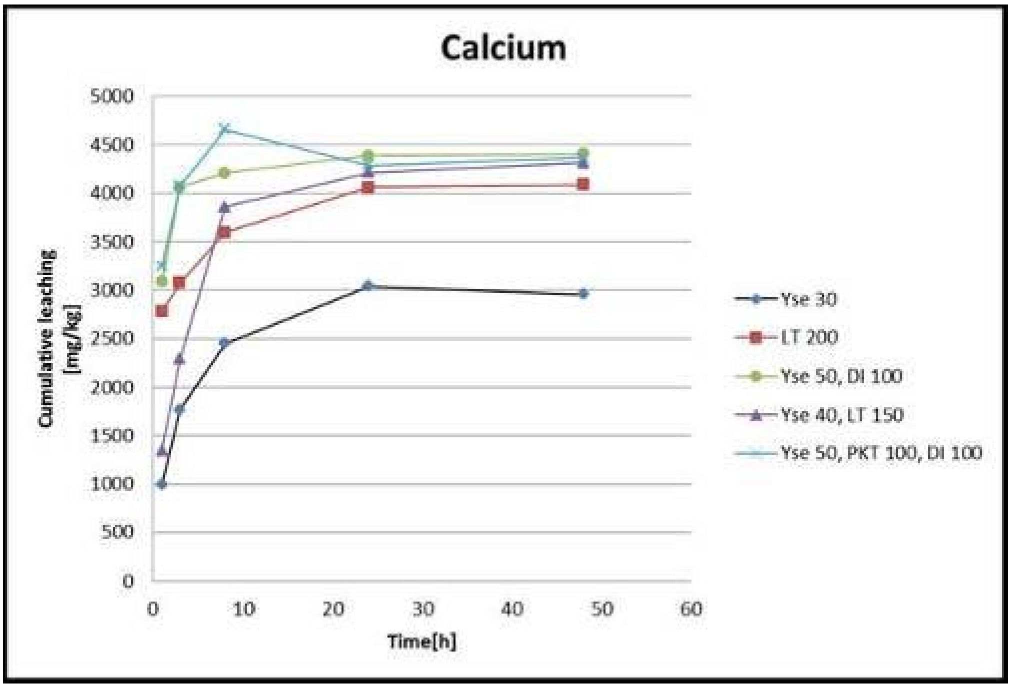

Figure 4.100 Calcium leaching from stabilized material during batch testing

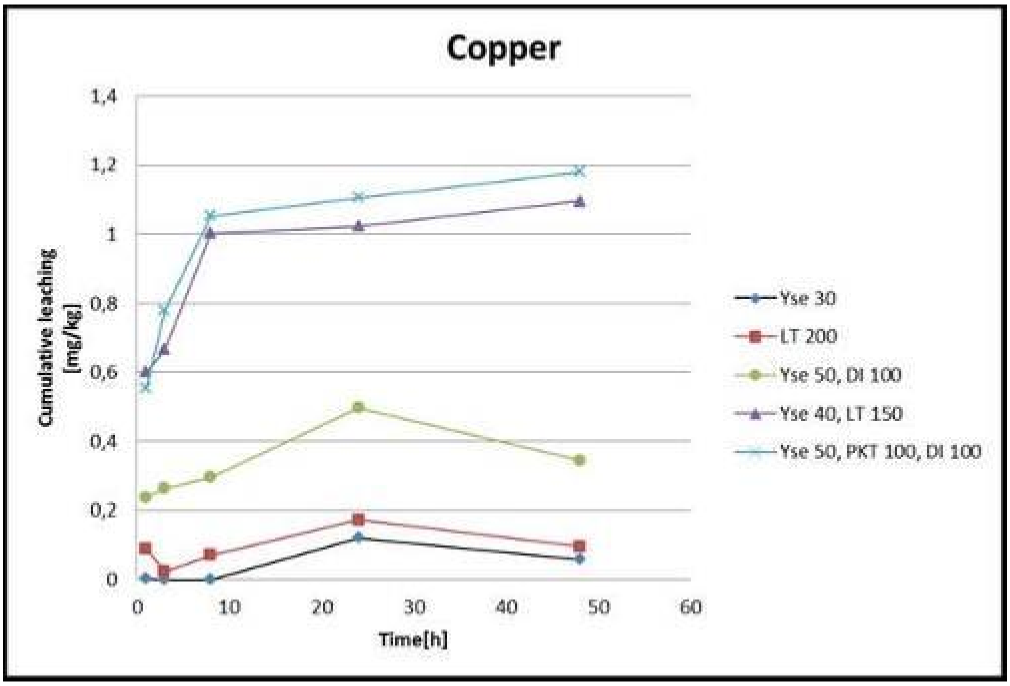

Figure 4.101 Copper leaching from stabilized material during batch testing

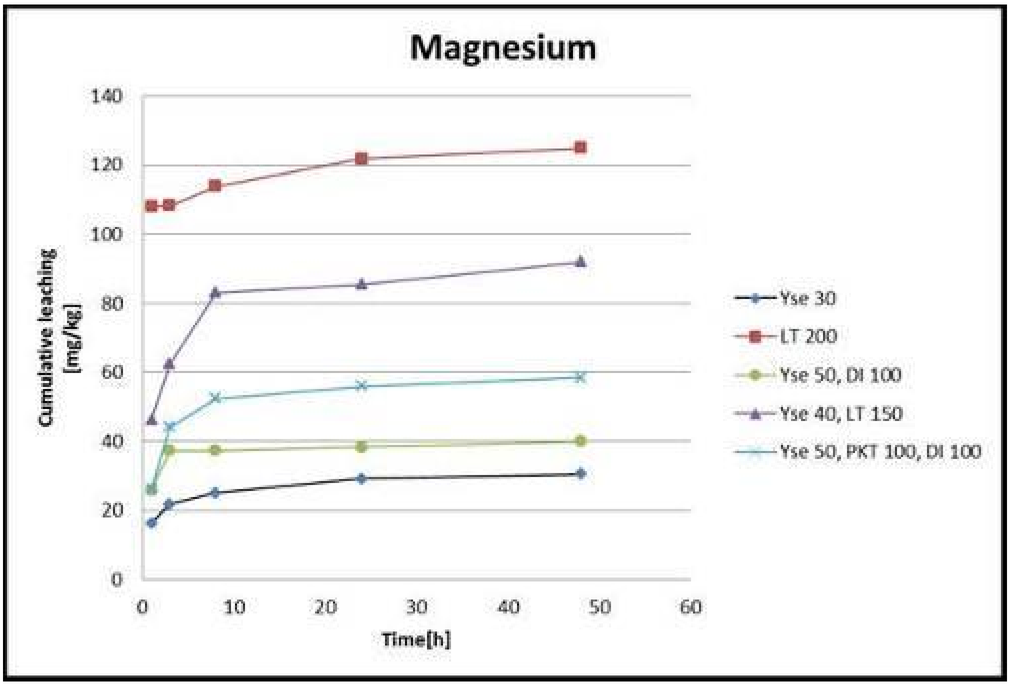

Figure 4.102 Magnesium leaching from stabilized material during batch testing

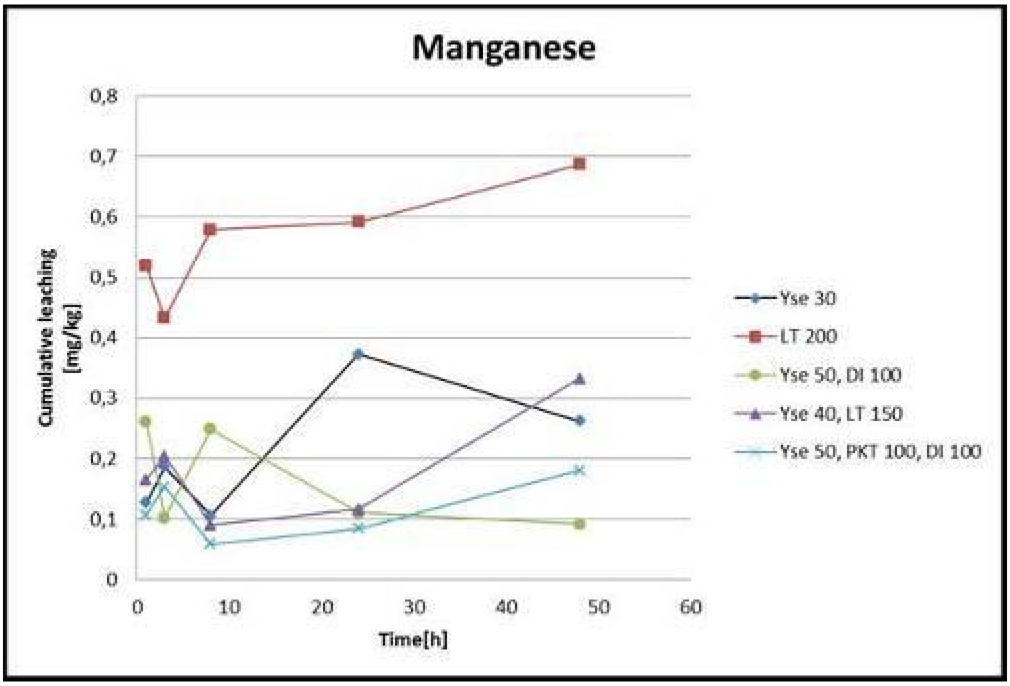

Figure 4.103 Manganese leaching from stabilized material during batch testing

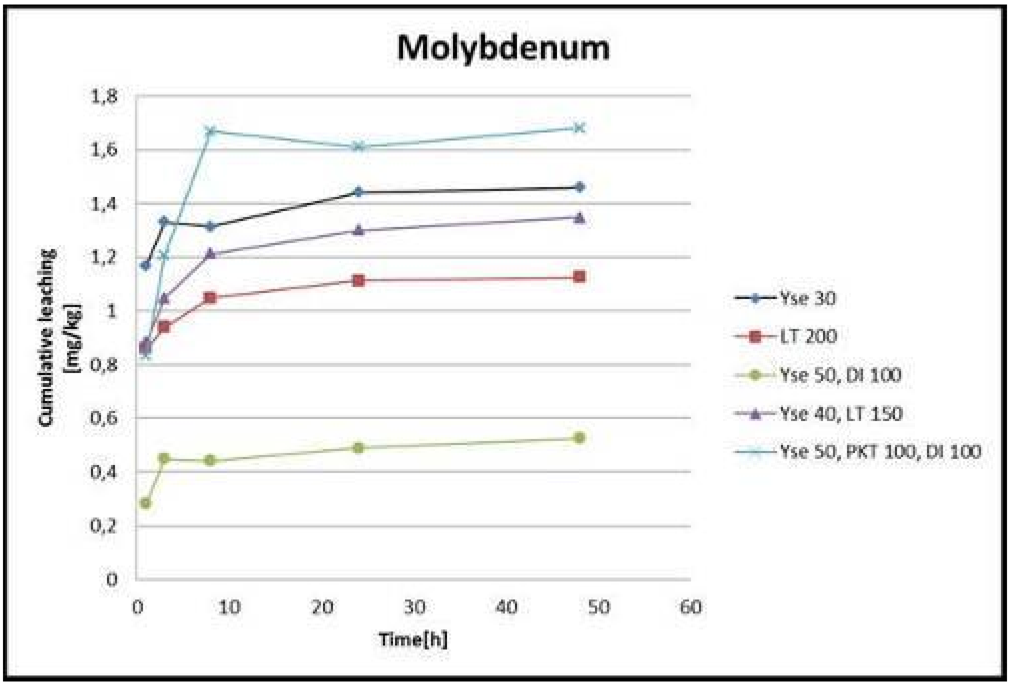

Figure 4.104 Molybdenum leaching from stabilized material during batch testing

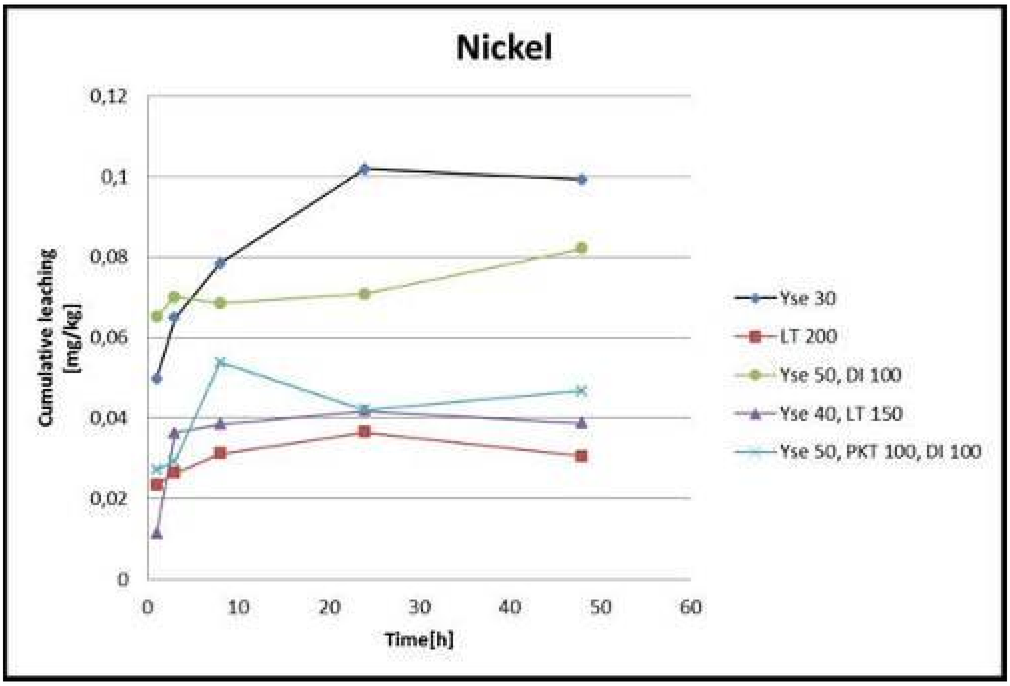

Figure 4.105 Nickel leaching from stabilized material during batch testing

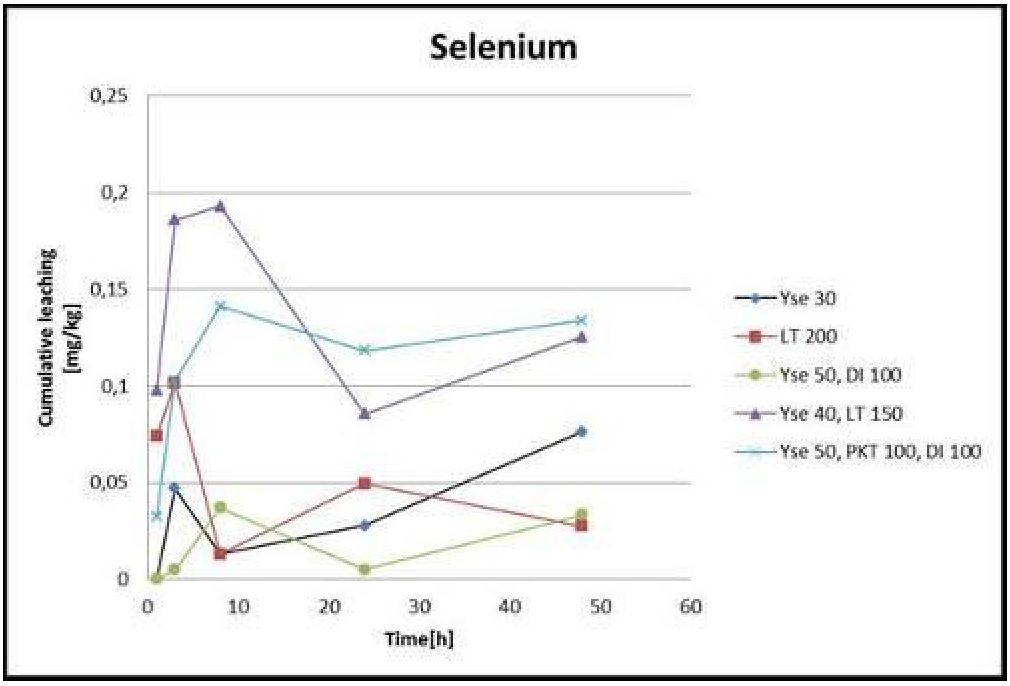

Figure 4.106 Selenium leaching from stabilized material during batch testing

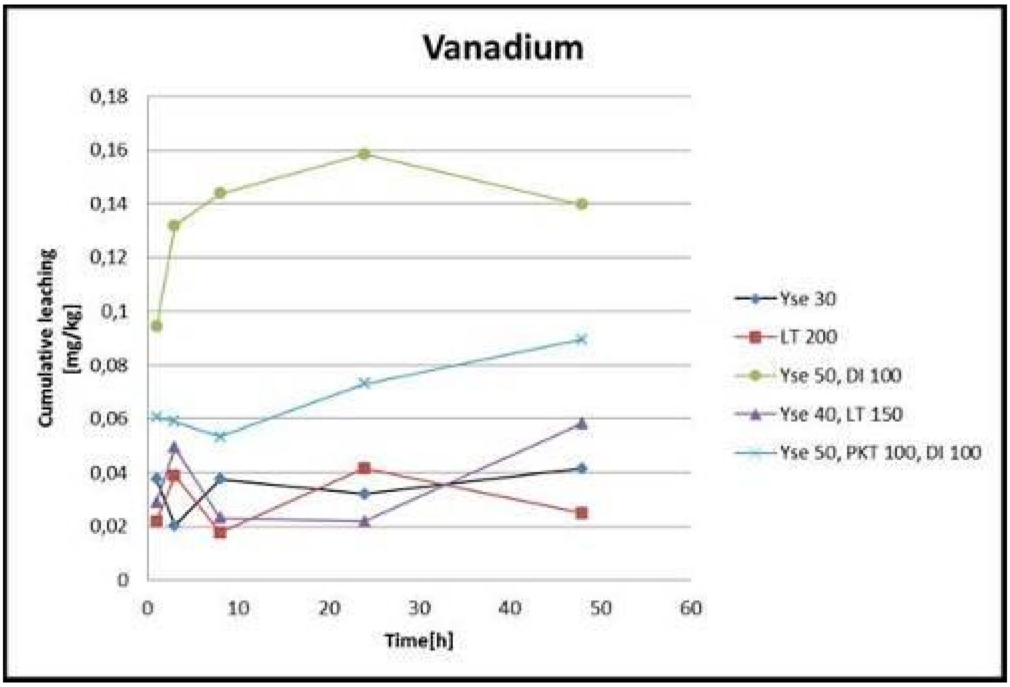

Figure 4.107 Vanadium leaching from stabilized material during batch testing

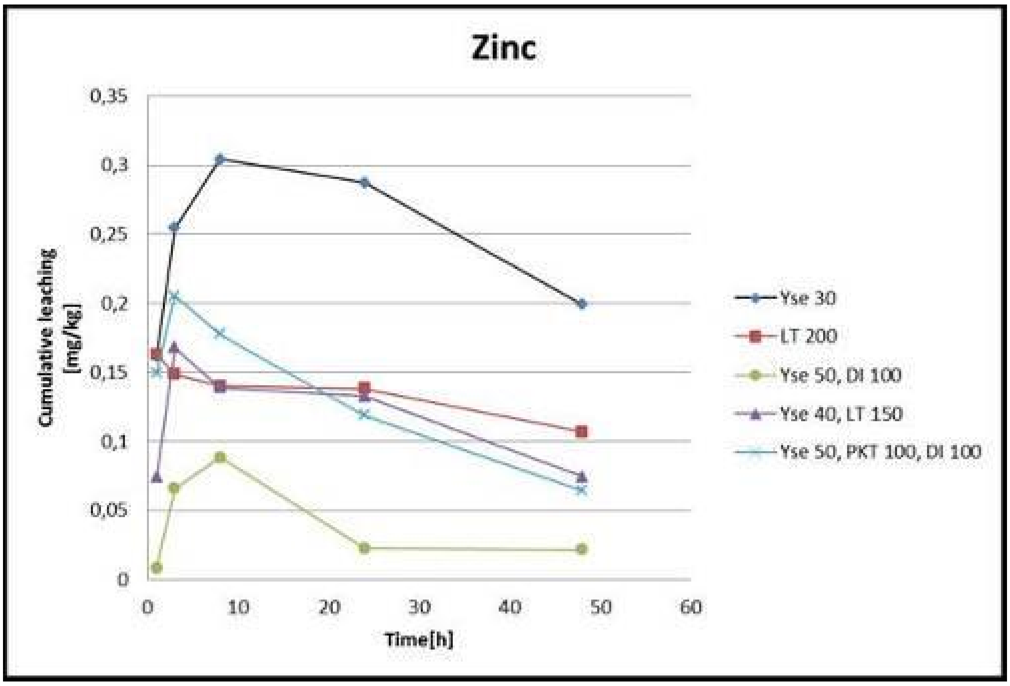

Figure 4.108 Zinc leaching from stabilized material during batch testing

5. Conclusions and Recommendations

Stabilization of contaminated sediments is highly dependent on a) sediment matrix, b) contamination, c) binder materials, and d) physical conditions including pH, temperature, pressure and water content.

By comparing different binder materials, easily over 95 % reduction can be achieved for some metals, e.g., Hg, Mg, and Zn assuming there is significant contamination in the sediment. Some metals, e.g., Cu, Fe, and Ni the reduction can be poor and the stabilization mechanism is not straight forward. Binder materials can also be a significant source of these contaminants. Considering nickel, it was detected that by applying gypsum of fly ash, the leaching could be decreased.

In each case based on the results, 2-stage batch test after 14 days stabilization period with heat treatment is recommended. Index properties of sediment should be carefully taken into account as well as properties and chemical composition of binder materials. SEM imaging can give a nice insight on the stabilization process.

For EU-level unified guidelines for management of contaminated sediments is currently lacking, but should be urgently formed. For unified analytical procedure guideline for evaluating environmental applicability, current international and national standards could be utilized, Appendix 1. Even though analytical standards exist, guideline limit values for leaching of contaminants as well as for total concentrations do not exist on international level. For instance, in Finland these limits are set on national level by the decree of government, which helps local authorities in environmental permitting. HELCOM has set guideline values that could be used as a background for the unified guideline.

Acknowledgements

The authors wish to thank European Union Baltic Sea Region Programme, Eesti Energia AS, Yara Suomi Oy, and Centre for Economic Development, Transport and the Environment of South-Eastern Finland for financial support. Cooperation with Port of Kokkola, Port of Gävle, Port of Gdynia is highly appreciated. Maritime Institute in Gdánsk, Luleå Technical University, Coastal Research and Planning Institute of Klaipeda, and Technical University of Hamburg are acknowledged for their valuable input in scientific network. Particularly the authors wish to thank Göran Holm and Swedish Geotechnical Institute for the coordination in the project.

Appendix 1

List of analytical standards

	Standard	Used at:	Notes
LEACHING TESTS			
Two-step batch test	SS-EN 12457-3	SGI, Sweden LUT, Finland	L/S 2 and L/S 10. Used for both sediment and stabilised sediment.
Static Diffusion test	NEN 7345	SGI, Sweden	Used only for monolithic stabilised sediment. According to standard the sampling and analysis of leachate shall be performed during 8 times, that is after total 6 hour, 1 day, 2 days, 4 days, 8 days, 16 days, 32 days, 64 days. The method used at SGI (STABCON project) is somewhat modified. Sampling performed according to standard but 4 compiled samples are analysed: 6h + 1d, 2d + 4d, 8d + 16d, 32d + 64d. Leaching liquid are sometimes changed to sea water, tap water etc, in order to imitate full scale. In case of organic analysis, the test equipment is made of glass and covered with alumina foil during test, the leachates are centrifuged (< 045 µm) and the samples are stored to minimize degradation.
Static Diffusion test	NVN 7347	SGI, Sweden LUT, Finland	Used only for sediment. The method used at SGI in STABCON project is somewhat modified: Modification the same as described above for NEN 7345. Additionally, the leachable surface of the sediment is covered with glass pearls (organic analyses) or plastic pearls (inorganic analyses), to 20 mm height.

Dynamic Diffusion test	Draft standard WI 00292056 CEN/TC 292/WG 6 N486	SGI, Sweden	Used only for monolithic stabilised sediment. Flow velocity of the leachate is adjusted in order to obtain total of L/S 10 during min 40 days – max 50 days. Minimum 3 samples are taken out for analysis (for ex. L/S 2, L/S 5, L/S 10) in order to obtain comparable data (for ex. two-step batch test).
Static pH Leaching Test		SGI, Sweden	
CHEM ANALYSIS			
pH	ISO 10390:2007	SGI, Sweden LUT, Finland	
Electric conductivity	ISO 11265		
TOC (Total organic content)	SFS-EN 13137	Not perfomed by SGI LUT, Finland	Performed by external lab
Inorganic content		Not perfomed by SGI	Performed by external lab: ICP-MS (Inductively Coupled Plasma – Mass Spect.)
16PAH		Not perfomed by SGI	Performed by external lab: HPLC (1 litre I glass bottle)
7PCB		Not perfomed by SGI	Performed by external lab: GC-ECD (1 litre I glass bottle)
	CEN 15308:2005	LUT, Finland	
Organic Tin compounds		Not perfomed by SGI	Performed by external lab: GC-AED (250 ml glass bottle)
Other organic		Not perfomed by SGI	Method and lab: Depending on selected organic
Metals (As, Ba, Cd, Co, Cr, Cu, Mo, Ni, Pb, Zn)	EN-ISO 11885 ISO 8288	LUT, Finland	ICP AAS
Ions (bromide, chloride, fluoride,	EN-ISO 10304-1	LUT, Finland	IC

nitrate, nitrite, phosphate, sulfate)	EN-ISO 10304-2 SFS-EN 12506		
Determination of total residue and total fixed residue in water, sludge and sediment	SFS 3008	LUT, Finland	
GEOTECHNICAL			
Classification, grain size distribution		SGI, Sweden	
Density	CEN ISO 17892-2	SGI, Sweden	
Water content	CEN ISO 17892-1	SGI, Sweden	
Liquid limit	CEN ISO 17892-12	SGI, Sweden	
Organic content (LOI)	EN 15169:2007	SGI, Sweden	
Strength (un-drained shear strength): Fall-cone test	CEN ISO 17892-6	SGI, Sweden	
Strength (un-drained shear strength): Unconfined com-pression	CEN ISO/TS 17892-7:2005	SGI, Sweden	

Appendix 2

Intended for
Eesti Energia

Document type
Research report

Date
11.10.2012

STABILISATION OF SEDIMENT BY USING OIL SHALE FLY ASH AS BINDER
EESTI ENERGIA

Open your mind. LUT.
Lappeenranta University of Technology

Check	
Date	19/04/2012
Made by	Tarja Niemelin Noora Lindroos Jarno Kohonen Satu-Pia Reinikainen Heli Sirén
Checked by	LUONNOS
Approved by	

Ref	82128370-06

CONTENTS

APPENDIX

1. INTRODUCTION

The purpose of the stabilization tests has been studying of the potential of oil shale fly ash from Eesti Energia as binder in stabilization of sediments. The sediment materials which have been included in the studies are from West harbor in Helsinki in Finland; from Port of Kokkola in Finland; from River Kymi in Finland; from Port of Klaipeda in Lithuania and from Port of Gdynia in Poland.

The studies have been carried out as part of the SMOCS-project (Sustainable Management of Contaminated Sediments), in which the stabilization properties and effects of different binders on stabilization of Baltic Sea sediments have been studied among other things.

In this report following issues have been reported:

- Geotechnical index properties of sediment samples
- Strength development in an early stage
- Long term strength development
- Effect of water content of sediment on strength
- Optimization of binder recipes that is quantity and quality of binders used

Stabilization studies in different cases have proceeded to different stages. In most cases only preliminary results (Gdynia, Klaipeda, River Kymi) are available from stabilization studies. In Port of Kokkola and Jätkäsaari the studies have proceeded further.

Binders used in the studies are different cement qualities, lime, blast furnace slag, oil shale ash qualities of Eesti Energia and gypsum from Yara Finland Ltd.

Stabilization studies have been performed in the laboratory of Environmental Geotechnics of Ramboll Luopioinen in Finland and chemical analyzes in Ramboll Analytics.

2. OIL SHALE FLY ASH OF EESTI ENERGIA

Oil shale fly ash is produced from combustion of oil shale. Oil shale is sedimentary rock formed on the bottom of lakes and seas 400-450 million years ago. Oil shale contains kerogen which is a mixture of organic material. The significant feature of oil shale organic matter is its low solubility in strong solvents.

Utilisation and land filling suitability statement has been done for oil shale fly ash sample (Utilisation and land filling suitability of the fly ash of Narva, Ramboll Analytics Oy, 3.12.2010). Based on total contents oil shale fly ash is classified as regular waste in Finland and based on leaching test results the oil shale fly ash is suitable for placing to the landfill for a regular waste.

The total concentrations and leaching properties of an oil shale fly ash sample are shown in tables 1 and 2 respectively. The results are compared to the limit values of utilisation in earth construction purposes of ashes originating from burning of charcoal, peat and wood - originating material according to the Finnish Council of State's regulation 403/2009 "the Council of State's regulation of utilization of certain waste at earth construction to change the supplements 1 and 2".

The total concentrations of certain elements and organic compounds are below limit values for utilisation (table 1). The leaching tests performed were two-step batch test and percolation test, but the percolation test was unfinished, because of clogging of the column. The results from two-step batch test show that the leaching of sulphate exceeds the limit value for coated structure and leaching of chloride, fluoride, chromium, lead and molybdenum exceed the limit values for covered structure.

Table 1. Total contents of the ash sample, in the unit mg/kg dry weight

Parameter	Ash sample	*403/2009; basic research, ashes of burning
Arsenic	29	50
Barium	170	3 000
Cadmium	0,48	15
Chromium	45	400
Copper	<10	400
Lead	71	300
Molybdenum	9,4	50
Zinc	96	2 000
Vanadium	44	400
PAH	<1	20/40**
PCB	<0,01	1,0

*the Council of State's regulation 403/2009 of changing the supplements of the Council of State's regulation (591/2006) of utilization of certain waste at earth construction; **covered/coated structure

Table 2. Results from two-step batch test in L/S-ratio of 10 and results from percolation test in L/S-ratio of 2,9 (the test was aborted because of the clogged column) and the limits of regulation 403/2009 for covered and coated structure. The results are presented in unit mg/kg dry content.

Parameter	Ash sample, two-step batch test, L/S=10	Ash sample, percolation test, L/S=2,9	403/2009 covered structure*, ashes of burning	403/2009 coated structure*, ashes of burning
DOC	12,6	17	500	500
Chloride	1 200	2 900	800	2 400
Fluoride	18	3,5	10	50
Sulfate	16 000	5 100	1 000	10 000
Antimony	<0,020	<0,020	0,06	0,18
Arsenic	<0,020	<0,020	0,5	1,5
Barium	3,7	1,1	20	60
Mercury	<0,003	<0,003	0,01	0,01
Cadmium	<0,020	<0,020	0,04	0,04
Chromium	1,7	0,53	0,5	3,0
Copper	<0,020	<0,020	2,0	6,0
Lead	0,58	0,16	0,5	1,5
Molybdenum	1,9	1,4	0,5	6,0
Nickel	<0,020	<0,020	0,4	1,2
Selenium	<0,020	<0,020	0,1	0,5
Zinc	0,027	<0,020	4,0	12
Vanadium	<0,020	<0,020	2,0	3,0

*the Council of State's regulation 403/2009 of changing the supplements of the Council of State's regulation (591/2006) of utilization of certain waste at earth construction.

3. LABORATORY METHODS

Short descriptions of geotechnical tests used in stabilisation studies are presented below:

- The water content of a material (w) is the ratio of the quantity of water removed from the wet material (m_m) in the course of drying in an oven up to a constant mass value and the dry material mass (m_d). The general drying temperature is 105 °C for most of the samples.

- Loss of Ignition (LoI) will describe the content of the organic matter of the material. This can be characterized by the weight loss a dried material sample (m_d) will suffer in the course of heating as the organic matter will be combusted and lost at a very high temperature (550 / 800 °C for at least 1 hour). The residual mass is m_i. This weight loss is expressed in dry weight percentage, and called Loss of Ignition (LoI).

- Particle Size Distribution will be determined by a sedimentation tests. In a sedimentation test, or the areometer test, the grain size is determined on the basis of the settling rate of the particles in a liquid (according to Stokes' Law). The settling rate is measured by a specific gravity hydrometer, which is placed on a prefabricated solution on certain intervals.

- pH is determined by mixing 10 g of dry sample with 50 g of water and letting it settle for 2-4 hours. After settling the solution is mixed again and the pH is measured with the pH instrument.

- Active lime test is done according to standard SFS 5188. 0,5 g of ash is mixed with 10 ml of water and the mixture is heated on a stove to hydrate the lime. After the lime hydration 20 g of sugar is mixed to the cooled solution. After 15 minutes of reaction time the indicator phenolphthalein is added to the solution. The solution is titrated with hydrochloric acid. The amount of active lime in the ash is calculated with the equation below.

$$X = \frac{0{,}5 \cdot 56 \cdot 100}{1000} \cdot \frac{c \cdot V}{m} = 2{,}8 \cdot \frac{c \cdot V}{m}$$

  where:
  X is the amount of active lime, %
  V is the volume of spent hydrochloric acid, ml
  m is the mass of the sample, g
  c is the concentration of the hydrochloric acid, mol/l

- Preparation of test pieces. Sediment and binder(s) are mixed together by using laboratory mixer with constant mixing time of 2 minutes. Sediment-binder mixture is then compacted in cylinder shaped form. The size of the cylinder for 1-axial compression strength test piece and for water permeability test piece is *Φ* 42 mm, *h* 100 mm and *Φ* 103 mm, *h* 110 mm respectively. Normal storage temperature for specimens is +20 °C for the first two days and after that +8 °C until the specimen is tested. Elevated storage temperature is used if accelerated strength development is required. In that case samples are stored at the elevated temperature of +30 °C until tested. Vertical load is not used during curing time. Drying of test samples during storage is prohibited by packing them to plastic bags. After storage a test piece is removed from the form and the ends of the test piece are leveled to match the test specimen size of the UCS test of *Φ* 42 mm and *h* 84 mm.

- Unconfined Compressive Strength, UCS, is a standard test where a cylindrical test piece is subjected to a steadily increasing axial load until failure occurs. The axial load is the only force or stress applied. The rate of the load is 1 mm/min. If any noticeable failure does not occur, the maximum value of the compression strength is taken when the deformation (change of height) is 15 %.

- Soft wall permeability test with constant pressure is carried out according to the recommendations of the Environment Centre of Finland. A test piece inside a rubber membrane will be subject to a 3-dimensional pressure in a test cell. Water will be conducted through the test piece from a front container to a back container, and the water level differences of the containers will be measured. Water flows upward inside the test piece when there is higher pressure in the front water container than in the back container. The simple formula to calculate the water permeability factor is as follows:

$$k = \frac{Q * L}{A * t * H},$$

  where
  k = water permeability [m/s]
  Q = quantity of water seeping through a test piece [m^3]
  L = height of the test piece [m]
  A = area of the cross-section of the test piece [m^2]
  t = time [s]
  H = hydraulic differential pressure [m]

4. BINDERS

Table 3. Commercial binders used in stabilisation tests

Abbreviation	Name	Supplier	Other information
Pika	Rapid cement	Finnsementti	CEM I 52,5 R
Yleis / YSe / Cem	Ordinary Portland cement	Finnsementti	CEM II/A-M(S-LL) 42,5 N (no more available)
PeSe	Composite Portland cement	Finnsementti	CEM II/B-S 42,5 N (no more available)
KJ / K400	Blast furnace slag	Finnsementti	

Table 4. Industrial by-products used in stabilisation tests

Abbreviation	Name	Supplier	Other information
DI / KI / kipsi	gypsum	Yara Suomi Oy	Pile stored di-gypsum
PKT / OSA	oil shale ash	Eesti energia	Electric filter ash, old burning technology
PKT c	oil shale ash	Eesti energia	c = cyclone ash, old burning technology
PKT ba	oil shale ash	Eesti energia	ba = bottom ash, new burning technology, Eesti Power Plant, Block 8
PKT ef	oil shale ash	Eesti energia	ef = electric filter ash I + II field after desoxy-filter, old burning technology

Table 5. Index properties of binders

Binder	w [%]	LoI [%]	pH	Active lime [%]
DI	15,5 (40 °C) 44,4 (105 °C)	1,7	4,7	-
PKT	0	3,3	12,9	28

5. WEST HARBOUR IN HELSINKI, JÄTKÄSAARI

5.1 Materials

Sediment sampling was performed from the Saukonpaasi area in April 2010. Sampling from the Saukonpaasi area was performed by Suomen Vesityö Oy. Samples were taken with grab bucket.

The geotechnical index properties for sediment samples are shown in table 6. A combined sediment sample consisting of samples P4 1-2 m + P5 2-3 m + P5 4.5-5.5 m in proportion of 1:1:1 was used in stabilisation tests. The binders which were used in the study are shown in table 7.

Table 6. Geotechnical index properties of sediment samples from Jätkäsaari

Sample	w [%]	ρ_m [kg/m^3]	LoI [%]	pH
4 / 1-2 m	119	1410	4,2	8,0
5 / 2-3 m	111	1420	4,1	7,9
5 / 4,5-5,5 m	86	1510	3,6	8,2

Table 7. Binders used in stabilisation tests

Abbreviation	Name	Supplier	Other information
PKT A	oil shale ash	Eesti energia	filter ash/I-field, old burning technology. EPP
PKTB	oil shale ash	Eesti energia	filter ash/II-field, new burning technology. EPP
PKT C	oil shale ash	Eesti energia	cyclone ash, old burning technol-ogy. EPP
YSE	Ordinary Portland cement	Finnsementti	CEM II/A-M(S-LL) 42,5 N
kipsi, DI	gypsum	Yara Suomi Oy	Pile stored di-gypsum

5.2 Results

The results from 1-axial compression strength tests are shown in appendix 1. The sediment material can be stabilised with fairly low amount of binder: for example having 200 kPa of compression strength after 28 days of curing time 25 kg/m^3 of cement + 50 kg/m^3 of PKT A is needed or alternatively 135 kg/m^3 of PKT A.

A comparison of different oil shale ash quantities and qualities are shown in figure 1. Significant differences between oil shale ash qualities can be seen. When 150 kg/m^3 of oil shale ash is used PKT B, PKT A and PKT C are in series with decreasing compression strength after 28 days or 90 days of curing time. Increasing of the amount of PKT A from 50 kg/m^3 to 200 kg/m^3 the compression strength increases linearly after 28 days of curing time. After 90 days of curing time compression strength increases steeply after the amount of PKT A has been raised higher than 150 kg/m^3. The results for test pieces stored at elevated temperature of +30 ºC show that there are still potential for long-term strength development after 90 days of curing time, since the thermal treated test pieces have higher compression strength results than test pieces with 90 days of curing time in +8 ºC.

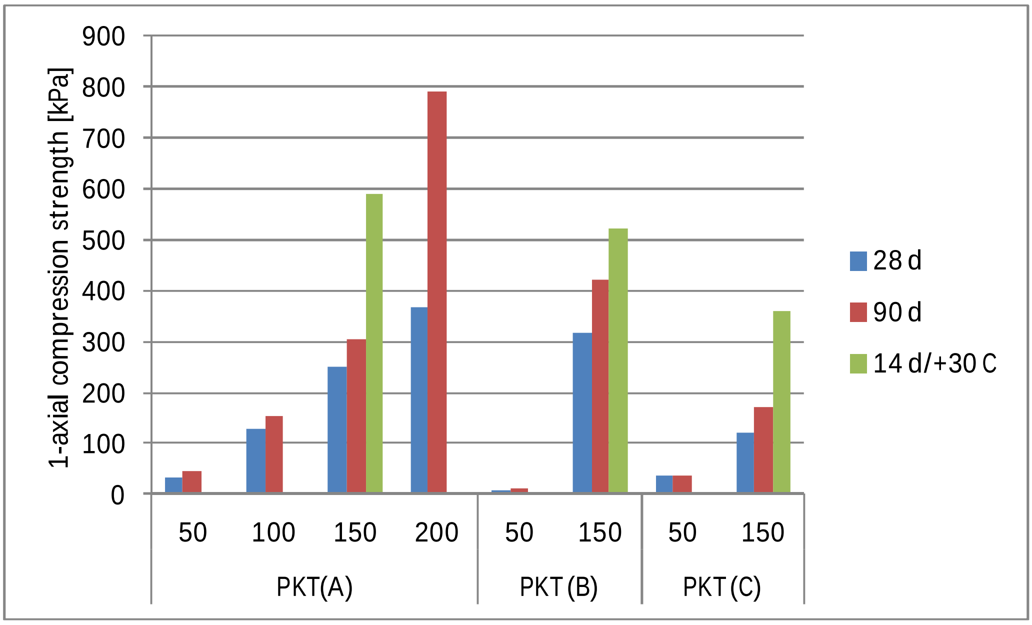

Figure 1. Effect of different OSA quantities and qualities on 1-axial compression strength (The units of the binder amounts are kg/m^3)

Compression strength results for cement-oil shale ash mixtures are shown in figure 2. Increasing the amount of cement or alternatively the amount of PKT A the compression strength increases significantly. The differences between compression strength results of different OSA qualities combined with constant cement amount are fairly small. The thermal treatment tests show that the binder mixture has a potential for long-term strength development.

Cement activation increases compression strength remarkably: for example compression strength is 155 kPa for 100 kg/m^3 of PKT A (figure 1); compression strength is 400 kPa for 20 kg/m^3 cement + 100 kg/m^3 of PKT A (figure 2).

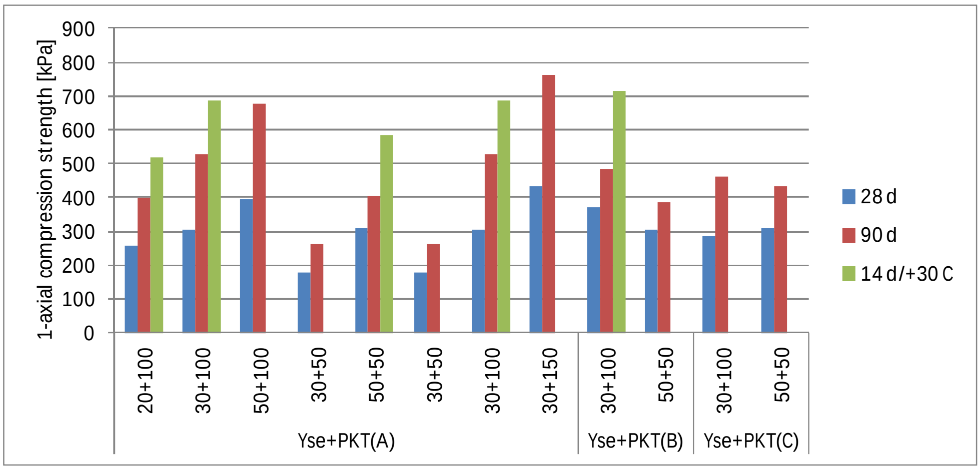

Figure 2. 1-axial compression strength results for cement-oil shale ash mixtures (The units of the binder amounts are kg/m^3)

Compression strength results are shown in figure 3 for cement-oil shale ash-gypsum mixtures. If compression strength results after 90 days of curing time are compared, binder mixtures with PKT A are most promising. The thermal treatment tests show that the binder mixture has a potential for long-term strength development.

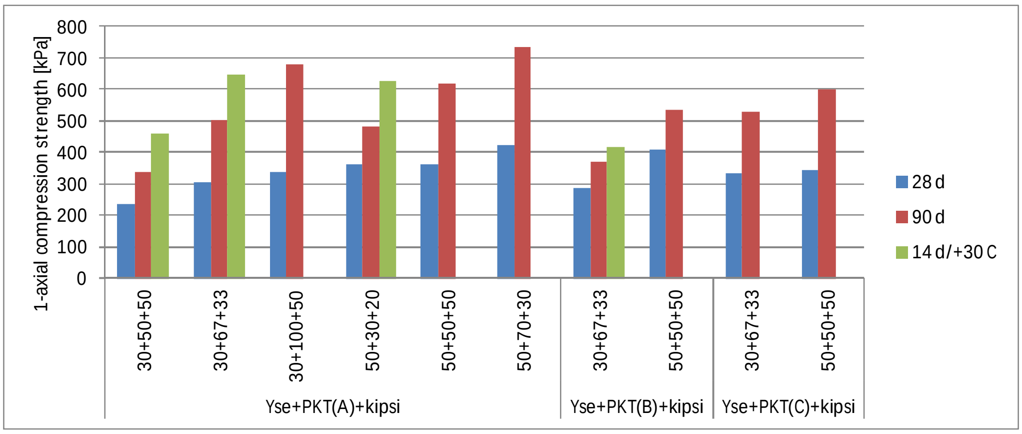

Figure 3. 1-axial compression strength results for cement-oil shale ash-gypsum mixtures (The units of the binder amounts are kg/m^3)

Comparison of cement-oil shale ash-gypsum mixtures and cement-oil shale ash mixtures are shown in figure 4. When the amount of cement is 30 kg/m^3 substitution of oil shale ash with gypsum does not bring additional strength but on the contrary it decreases the compression strength of the mixture. When the amount of cement is 50 kg/m^3 substitution of maximum 1/3 of the amount of oil shale ash with gypsum brings some extra strength to the mixture but if the amount of gypsum is higher the compression strength will decrease.

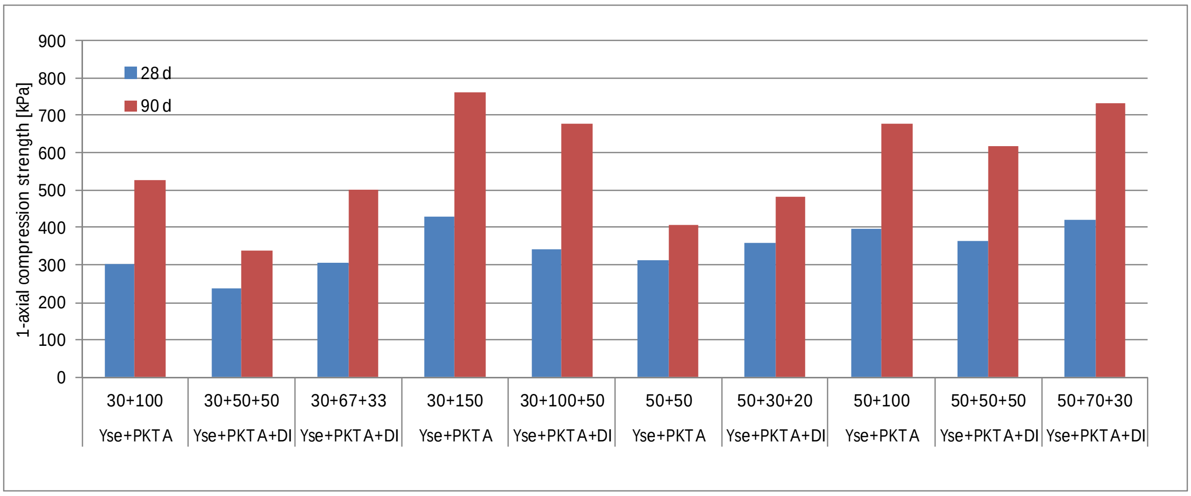

Figure 4. Comparison of cement-oil shale ash-gypsum mixtures and cement-oil shale ash mixtures (The units of the binder amounts are kg/m^3)

6. PORT OF KOKKOLA

Eesti Energia oil shale ash has been tested with sediments from Fairway of Kokkola and Kokkola Deep Port. Stabilization results from Fairway of Kokkola has been presented in report "Eesti Energia, Utilisation potential of oil shale ashes in the stabilisation of dredged sediments in the Port of Kokkola, Ramboll Finland Oy, 21.6.2011" and in chapter 5.2 is collected the most central results of that report. Chapter 5.4 focuses in Kokkola Deep Port sediment stabilization studies in which oil shale ash has been used.

6.1 Materials of Fairway of Kokkola

The stabilization tests were made for four (4) different sediment samples taken from the fairway of Kokkola. The characteristics of the sediments are represented in table 8.

Table 8. Sediment characteristics.

Sediment sample	water content [%]	Density ρ_m [kg/m^3]	Loss of ignition H_h [%]	Soil type
KS219 0-0,5m	153	1,34	3,7	muddy silt
KS213 0-0,5m	167	1,33	3,5	muddy silt
KS201 0-0,5m	52	1,71	1,5	silty loam
KS223 0-0,5m	120	1,42	2,1	silty loam

The stabilization tests were done with several different binder amounts and mixtures. The used binders were:

- oil shale cyclone ash, OSA C
- oil shale bottom ash, OSA BA
- oil shale electric filter ash, OSA EF
- Portland cement, Cem
- gypsum, Gyp.
- fly ash from combustion of mixed fuel (peat, wood, REF), FA

6.2 Results of Fairway of Kokkola

The stabilisation tests were done in three stages. The first two stages were done only with sample KS 219 0-50 cm and the last stage was done with three other sediment samples (KS 201, 213 and 223) to test the correspondence of the results with other sediment samples.

On the first stage Oil shale cyclone ash was used in the stabilization tests alone and together with cement, gypsum and fly ash. The specimens were thermally treated for 7 or 14 days. The results of the first stage are shown below in figure 5.

The thermal treatment results show that oil shale cyclone ash does not work as only binder component. Combination of oil shale ash with gypsum does not work. Compression strength results for cement-oil shale ash mixtures are low with tested binder amounts; the amount of cement or oil shale ash should be increased. The results for combination of cement, oil shale ash and gypsum show that the amount of cement have to be sufficient (at least 50 kg/m^3) in order to achieve reasonable strength. Increasing the amounts of oil shale ash or gypsum in the mixture does not bring benefit if the amount of cement is too low. Combination of four binder components, cement, fly ash, oil shale ash and gypsum, give low compression strength results with tested binder amounts.

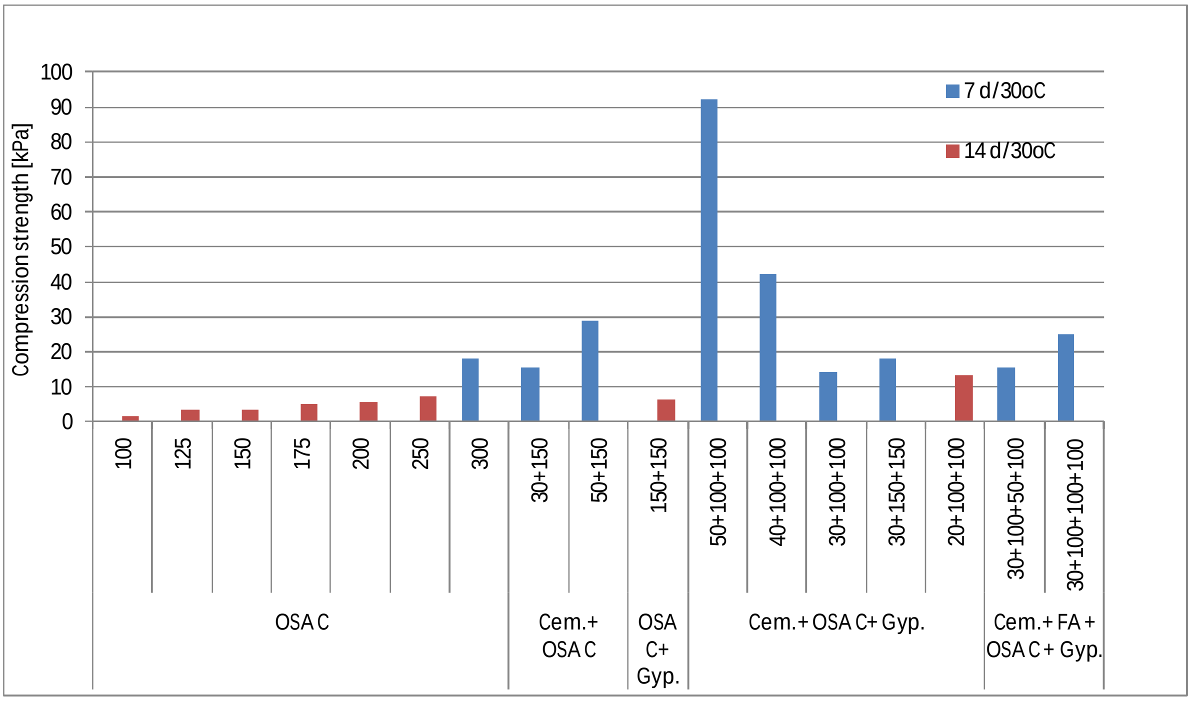

Figure 5. Results of the first stage stabilisation tests for KS 219 0-50 cm (The units of the binder amounts are kg/m[3])

On second stage different OSA materials were tested together with other binders. Every binder mixture were thermally treated for 28 days and normally treated for 90 days. The results of the second stage of the stabilization tests are shown in Figure 6 below.

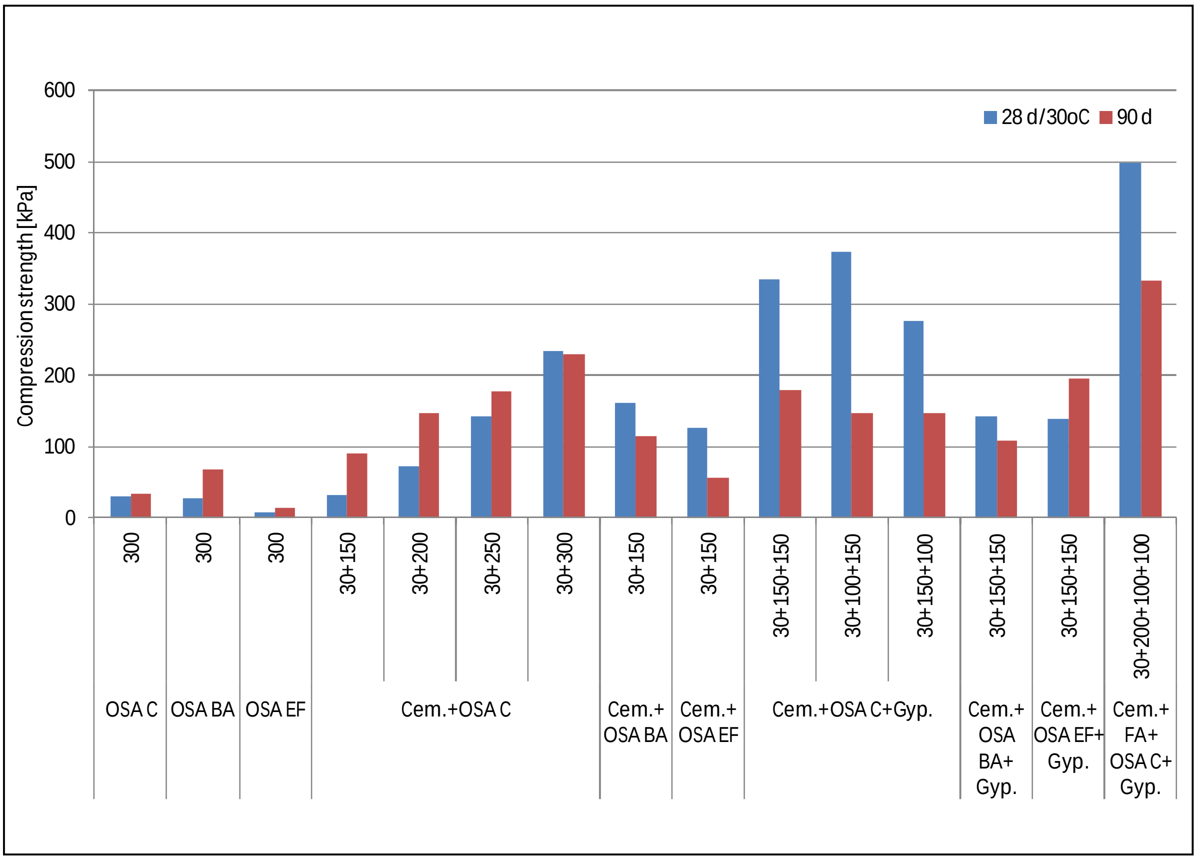

Figure 6. Results of the second stage of the stabilization tests for KS 219 0-50 cm (The units of the binder amounts are kg/m[3]).

Results show that the oil shale ash qualities do not work as only binder component, cement activation is needed. In cement-OSA C mixture increasing the amount of OSA leads to increase of compression strength. In cement-OSA binder mixtures after 90 days of curing time OSA BA gives better results than OSA C and OSA EF gives lowest compression strength value. Substitution of oil shale ash with gypsum in cement-oil shale ash-gypsum mixtures does not give benefit for samples tested after 90 days of curing time. In cement-OSA-gypsum mixtures OSA EF and OSA C give better result than OSA BA. With combination of cement, fly ash, OSA C and gypsum the compression strength is high but the amount of binders is high as well. Thermal treatment gives conflicting results; most reliable comparisons between different binders can be made from results after 90 days of curing time in normal treatment at +8 ºC.

On the third stage the different binder mixtures were tested with three other samples. The different binder mixtures were thermally and normally treated for 28 days. The results of the third stage of the stabilization tests are shown below in Figure 7.

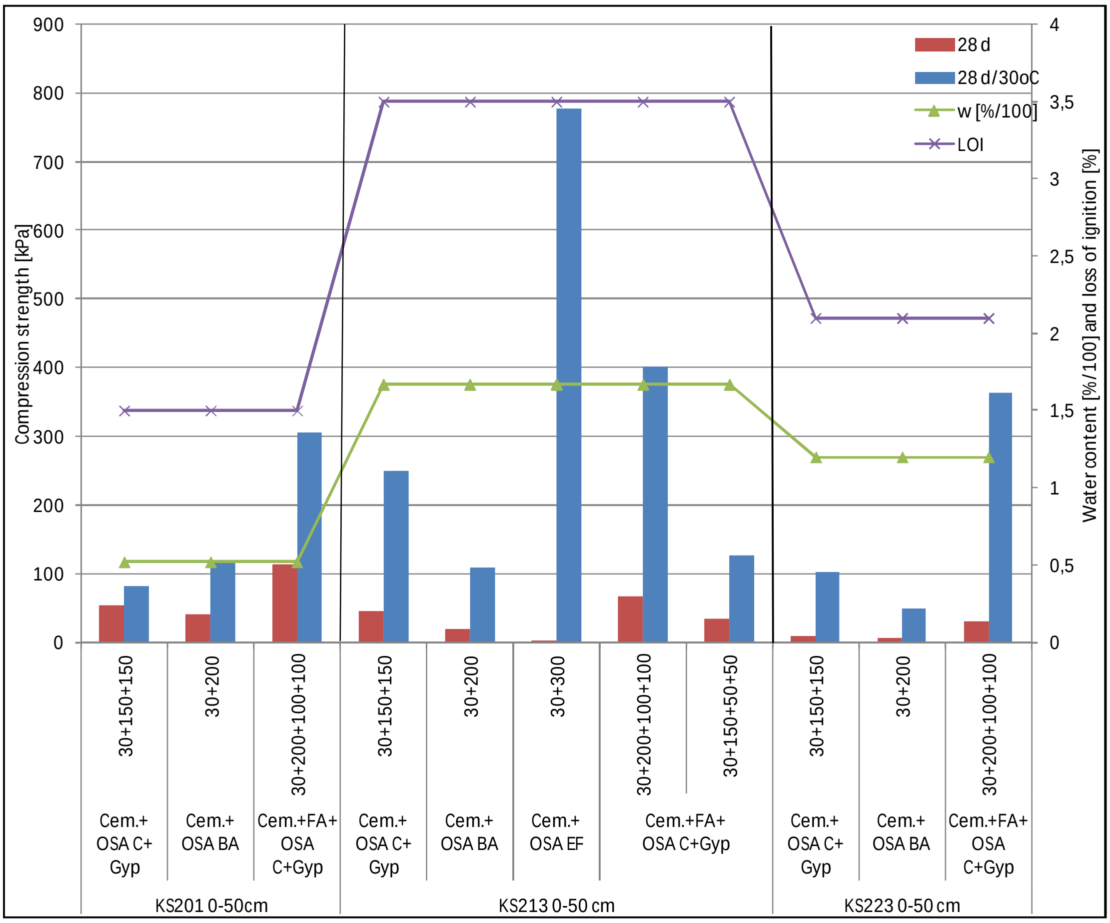

Figure 7. Results of the third stage of the stabilisation tests (The unit of the binder amounts is kg/m^3).

The figure 7 shows that according to the 28 d normally treated specimens the best compression strengths can be achieved with KS 201 0-50 cm, the second best results gave KS 213 0-50 cm and the lowest compression strengths gave the KS 223 0-50 cm sample. There is some consistency with water content and organic matter content of sediment samples with compression strength results; the sample with lowest water content and organic matter content had higher compression strength results than other samples with same binder combinations. Anyhow the sample with highest water content and organic matter content did not have lowest compression strength values. That is due to other differences between samples for example differences with grain size distribution or possible chemical contaminations in the samples, which can affect strength development.

6.3 Materials of Port of Kokkola, Deep port

The studied characterization tests were water content, density, loss of ignition, particle size distribution. The results are shown in table 8.

Table 8. Characterization of sediment samples.

Sample	w [%]	ρ_m [kg/m^3]	LoI [%]	Particle size
KS201+KS202	52	1700	1,3	silt
KS202	53	1700	1,2	silt
KS201	52	1700	1,5	silt

Binders used in stabilization were both commercial binders and industrial by-products. The used binders were

- Rapid Portland cement (Pika)
- Portland cement (YSe)
- Portland-Blast furnace slag cement (PeSe)
- Blast furnace slag (KJ)
- Gypsum (DI, kipsi)
- Oil shale ash, electric filter ash (PKT)

6.4 Results of Port of Kokkola

Cement-oil shale ash mixtures

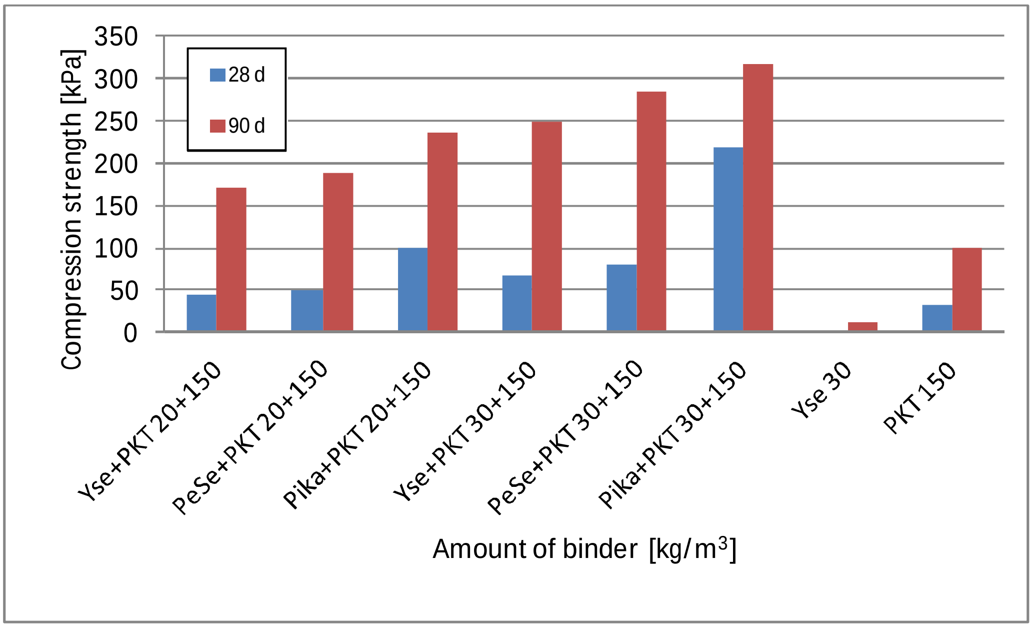

Figure 9. Functionality of different cements with oil shale ash.

- Best cement to function with oil shale ash is Rapid cement, then Portland-Blast furnace slag cement and Portland cement
- Strengthening reactions can be activated with small addition (20-30 kg/m^3) of cement when the strength raises remarkably compared to strength achieved by using only oil shale ash
- Time curing is significant

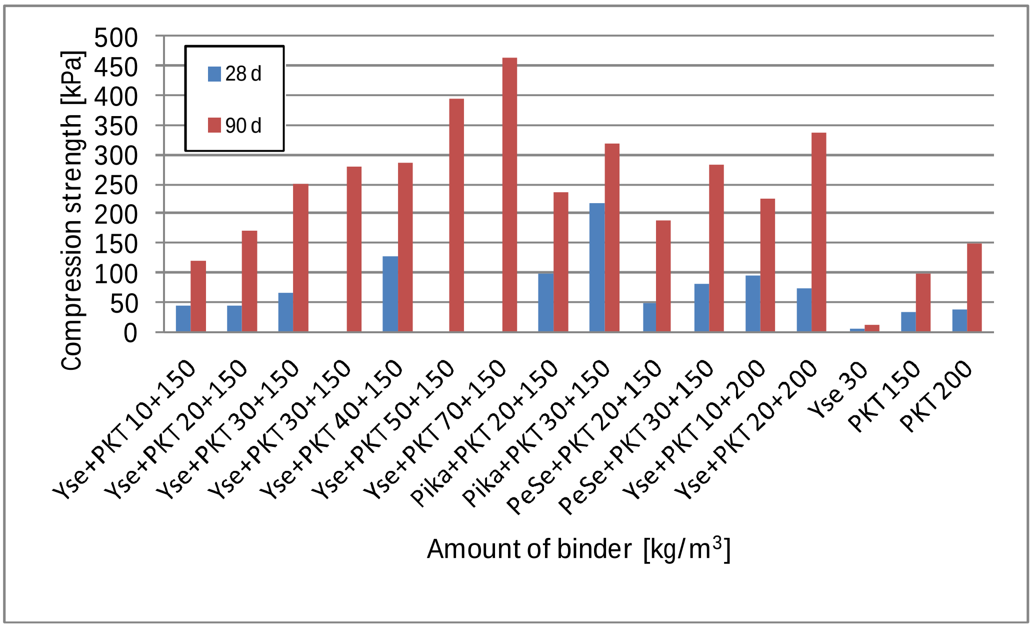

Figure 10. Effect of the amount of cement on compression strength in cement-oil shale ash mixtures.

- Increasing of the amount of cement has a clear influence on compression strength
- Strengthening reactions can be activated with small addition (20-30 kg/m^3) of cement when the strength raises remarkably compared to strength achieved by using only oil shale ash
- Time curing is significant

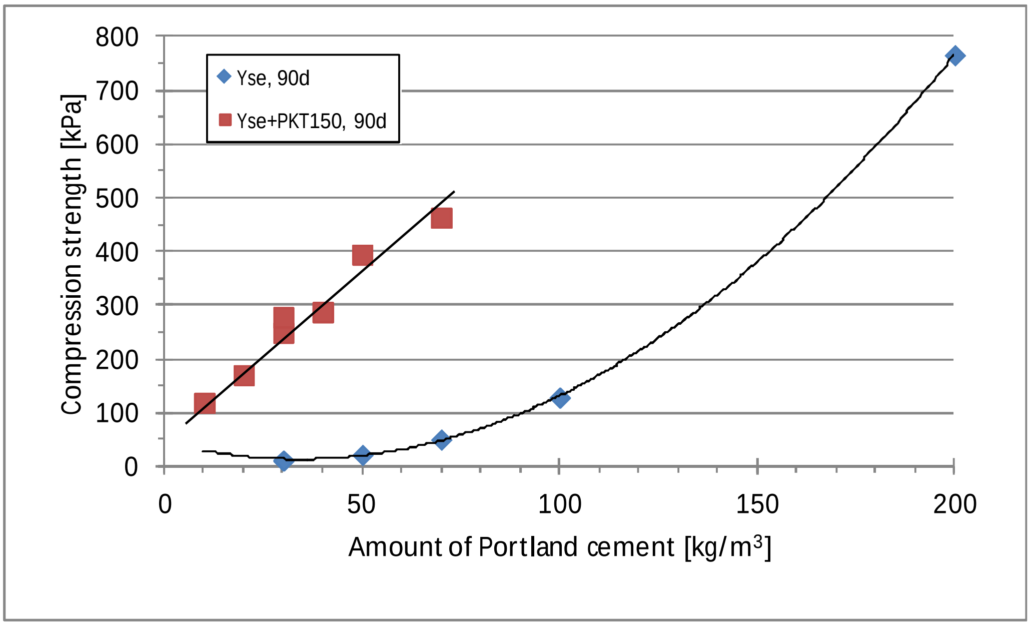

Figure 11. Replacing cement with oil shale ash

- It takes 100 kg/m^3 of Portland cement or 10 kg/m^3 Portland cement + 150 kg/m^3 oil shale ash to achieve 100 kPa strength (90 days)
- It takes 120 kg/m^3 Portland cement or 30 kg/m^3 + 150 kg/m^3 oil shale ash to achieve 200 kPa strength (90 days)
- The amount of Portland cement can be minimised by using oil shale ash as binder

Cement-oil shale ash-gypsum mixtures

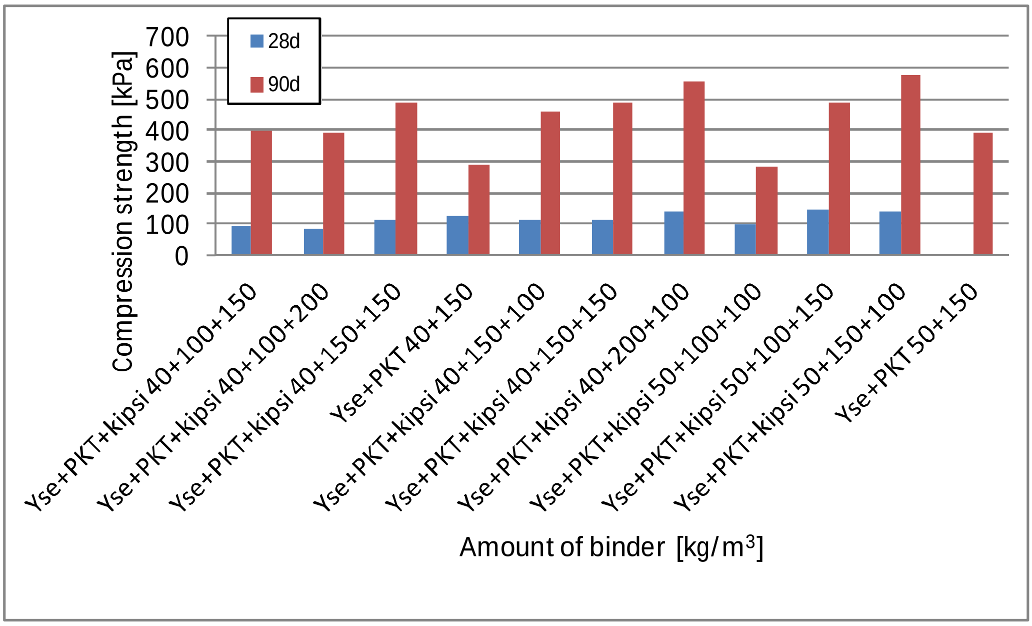

Figure 12. Compression strength of cement-oil shale ash-gypsum-mixtures

- Increasing the amount of oil shale ash is more effective than increasing the amount of gypsum in cement-oil shale ash-gypsum mixture
- Time curing is significant

Cement-blast furnace slag –oil shale ash-gypsum mixtures

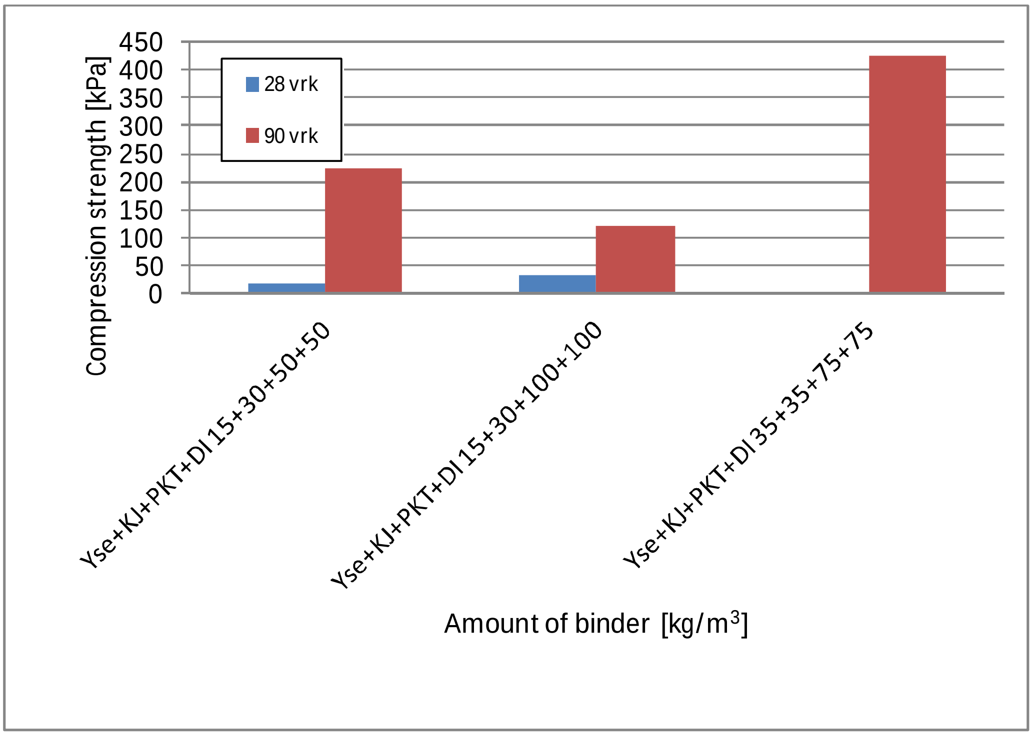

Figure 13. Compression strength of cement-blast furnace slag-oil shale ash-gypsum-mixtures

- Increasing of the amounts of oil shale ash and gypsum does not bring benefit

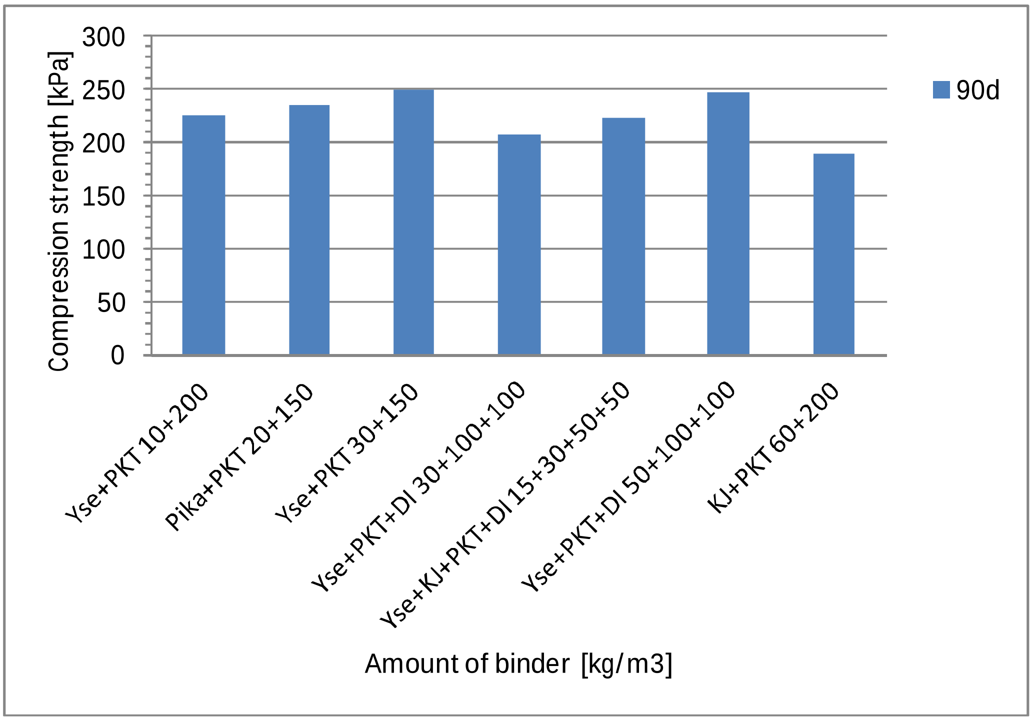

Figure 14. Binder mixtures to achieve 200-250 kPa strength in 90 days. The amount of commercial binder rises to the right.

- Target strength can be achieved with very low amounts of commercial binders

Effect of long-term strength development

Long-term strength development was studied with different binders: oil shale ash, YSe-gypsum-mixture, YSe-oil shale ash-mixture, YSe-oil shale ash-gypsum-mixture. Long-term strength development is shown in figure 15.

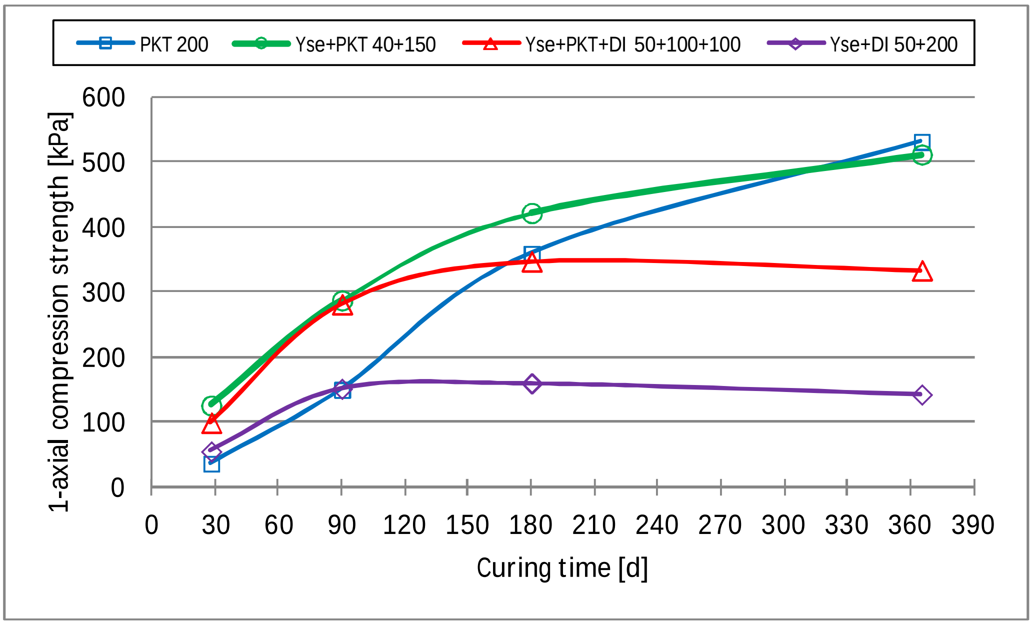

Figure 15. Effect of time curing.

- With oil shale ash and Portland cement-oil shale ash mixture the curing continues for one year
- Portland cement- oil shale ash-gypsum mixture reaches final strength in six months
- Portland cement- gypsum mixture reaches final strength in three months

7. RIVER KYMI

Sediments of River Kymi all the way from Kuusankoski to Gulf of Finland are contaminated with dioxins, furans and mercury. Total amount of PCDD/F-compounds is estimated to be 6000 kg and 2800 kg of mercury. The amount of contaminated sediment is estimated to be 5 million m^3. Contamination is not homogenous, but instead in slower points of stream the soft sediments are contaminated. In those parts where river bottom is hard and coarse, sediments are not contaminated. Flow of the river transports contaminants slowly towards the Gulf of Finland.

7.1 Materials

Sampling area is located in Kuusankoski Power Plant downstream. The samples were taken by diver with tube and shovel. The geotechnical index properties are shown in table 10. The organic matter contents of sediment samples were high. Sediment samples contain for example organic fibres originated from forest industry carried on by the river.

Table 10. Geotechnical index properties of sediment samples

Sample	w [%]	ρ [kg/m³]	LoI [%]	pH	Soil type
P1	351	1140	21,3	6,2	Gyttja
P2	274	1180	15,6	6,2	silty gyttja
P3	275	1180	14,0	6,3	silty gyttja
Kokooma P1-P3	296	1170	16,9	6,3	silty gyttja

The used binders in stablisation tests were:

- Cement (YSe)
- Oil shale ash (PKT A)
- Slag furnace powder (KJ)
- Di-gypsum from Yara Finland (DI)

7.2 Results

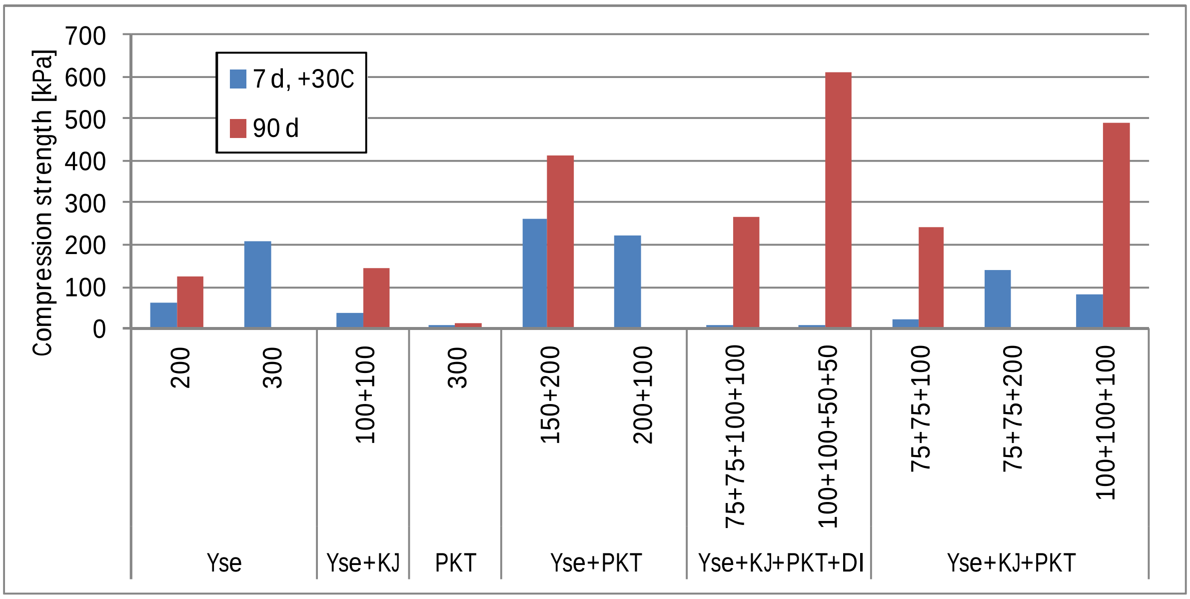

Figure 16. Compression strength results for sediment samples from River Kymi

Addition of 100 kg/m^3 of gypsum to cement-blast furnace slag-oil shale ash (Yse+KJ+PKT 75+75+100) does not bring extra strength to the mixture, whereas substitution of oil shale ash with gypsum in cement–blast furnace slag–oil shale ash-gypsum mixture (Yse+KJ+PKT 100+100+100 → Yse+KJ+PKT+DI 100+100+50+50) gives considerable extra strength to the mixture.

8. KLAIPEDA

Gypsum has been tested with sediments from Port of Klaipeda.

8.1 Materials

The results of characterization tests are shown below in Table 11. Samples nr 1 and nr 2 as well as samples nr 5 and nr 6 were combined as aggregate samples.

Table 11. Characterization tests of sediment samples.

Sample code	Water content [%]	Bulk density [kg/m^3]	Ignition loss [%]	pH	Soil type	Notes
139 / nr 1	248	1210	10,8	8,0	gyttja (sand)	pH and grain size measured from aggregate sample nr1+nr2
139 / nr2	279	1190	12,3			
65 / T3	131	1360	4,4	7,7	silty sand (humus)	
65 a / nr 4	70	1580	3,9	7,9	sand (humus)	
58 / nr 5	175	1290	7,7	7,8	silty gyttja	pH and grain size measured from aggregate sample nr5+nr6
58 / nr 6	142	1330	5,7			

Binders used in the stabilization tests are:

- Portland cement (Yleis)
- gypsum (KI)
- oil shale cyclone fly ash (PKT c)
- oil shale bottom ash (PKT ba)
- oil shale electric filter fly ash (PKT ef)

8.2 Results

Stabilization tests were done for 4 different sediment samples. Two of them were "main samples" to which 15 different binder recipes were tested. Samples were tested after 90 days of normal treatment (+8 ^{0}C) and after 4-6 and 28 days of thermal treatment (+30 ^{0}C).

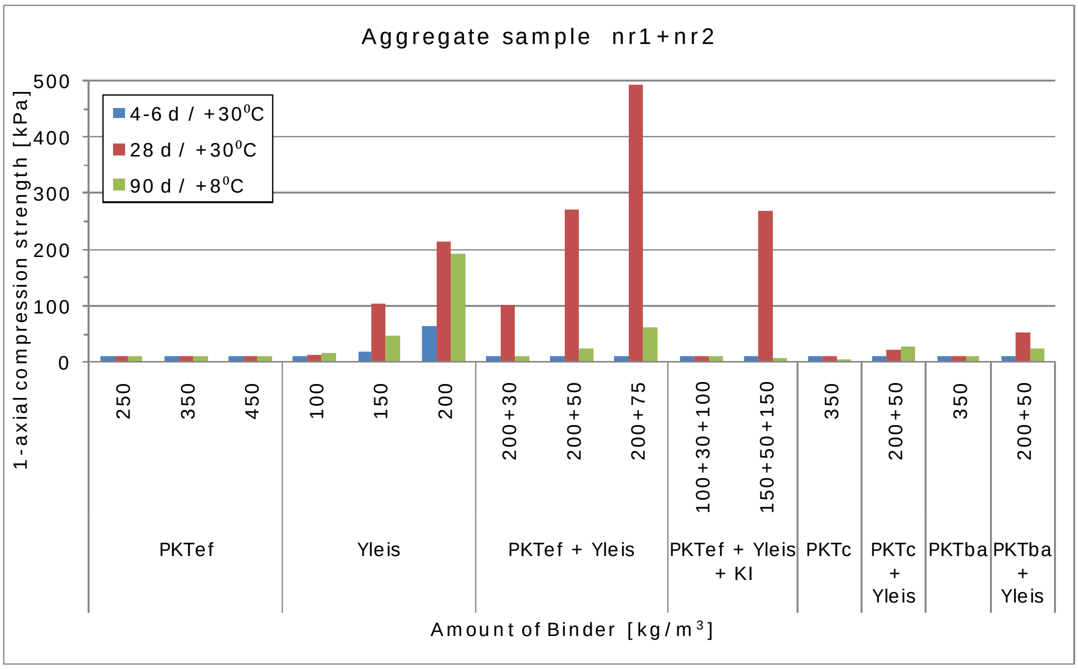

Figure 17. Results of stabilisation tests for aggregate sample nr1+nr2

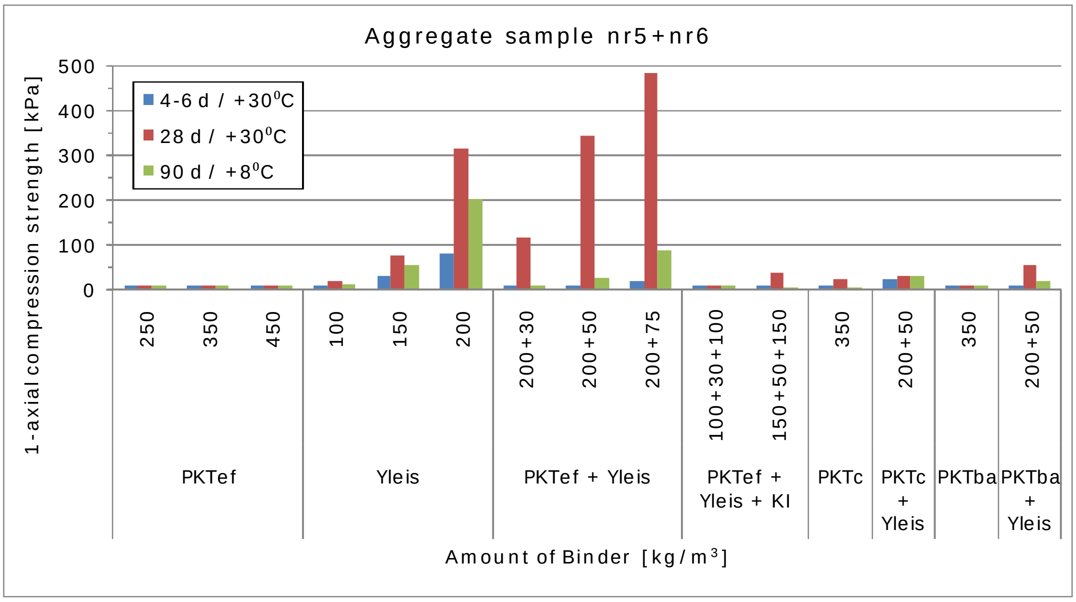

Figure 18. Results of stabilisation tests for aggregate sample nr5+nr6

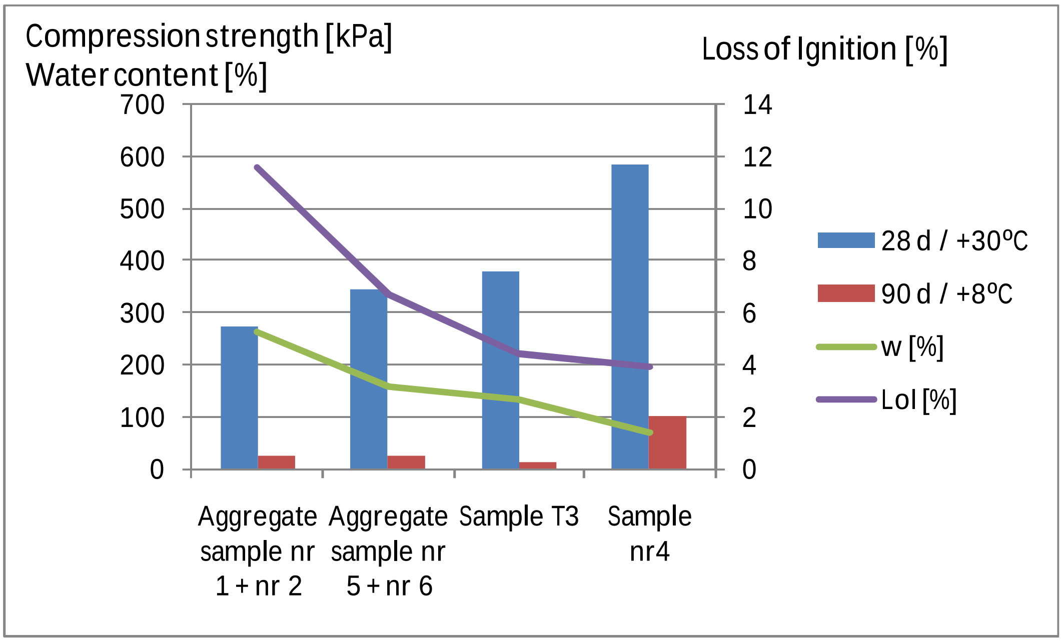

Figure 19. Effect of water content and organic matter content of samples on strength. Binder recipe is 50 kg/m3 cement (Yleis) + 200 kg/m3 oil shale ash (PKT ef).

The results show that:

- The amount of cement needed for stabilization is high; approximately 200 kg/m^3, if 200 kPa is the target level for 1-axial compression strength.
- Oil shale ash qualities are not working as binder material without cement activation. The amount of cement needed with oil shale ash is high. The tests were done using 30, 50 or 75 kg/m^3 of cement, which were too low amounts. In those recipes the strength was lower than 100 kPa after 3 months of curing time in +8 ^{0}C. Estimated amount of cement needed with oil shale ash is ≥100 kg/m^3 if 200 kg/m^3 of oil shale ash is used.
- 28 days of thermal treatment in +30^{0}C shows the long-term curing potential of the binder mixtures. In most recipes the strength in 90 days of normal treatment is much lower than the 28 days thermal treatment results. It means that the 28 days thermal treatment results predict the curing potential of recipes for much longer period of time than 3 months. Especially this is true for cement + oil shale ash binder mixtures; for cement binder mixtures the difference between 28 d/+30 ^{0}C and 90 d/+8 ^{0}C results are not so remarkable.
- 4-6 days of thermal treatment was too short curing time for most of the binder recipes
- According to 28 days thermal treatment results electric filter oil shale ash (PKTef) is working as a binder material with cement, but cyclone oil shale ash (PKTc) or bottom oil shale ash (PKTba) are not working as binder material for Klaipeda sediment.
- The higher water content (w) and organic matter content (LoI) of sediment sample, the lower is the strength of stabilized test piece.
- The contaminants of the sediment samples can have an effect on curing of sediment-binder mixtures. The samples tested in this study seemed to be contaminated with mineral oil. The content of contaminants was not investigated in this study, but the smell and the colour of the sediment samples suggested that samples contained oil.

9. GDYNIA

Oil shale ash has been tested with sediment sample from Port of Gdynia. The results from stabilisation tests are presented in report “Port of Gdynia, Stabilisation test report, 3/2011, Ramboll Finland Oy”.

9.1 Materials

The results of characterization tests of sediment samples are shown in Table 12. Aggregate sample was used as base material in stabilisation studies.

Table 12. Characterization tests of sediment samples.

Sediment sample	w [%]	ρ [kg/m^3]	LoI [%]	pH
GD 1.b6	167	1300	7,6	7,5
GD 2.b6	201	1250	9,2	7,4
GD 3.b6	171	1290	8,9	7,6
GD 4.b6	125	1380	6,6	7,7
GD 5.b6	100	1450	7,0	7,8
GD 6.b6	164	1300	9,1	7,6
GD 7.b6	167	1290	9,0	7,5
GD 9.b6	153	1310	7,7	7,5
Aggregate sample*	169	1290	9,0	7,5

* Aggregate sample is a combination of samples 1, 2, 3, 6, 7 and 9.

Following binders were used in stabilisation studies:

- Yse = Ordinary Portland Cement (CEM II/A-M(S-LL) 42,5 N)
- PKT = Oil shale fly ash from Eesti Energia (Estonia)
- KJ = Blast furnice slag (Finland)
- DI =Diphosphate Gypsum from Yara (Finland)

9.2 Results

The results for stabilisation studies are shown in figure 20.

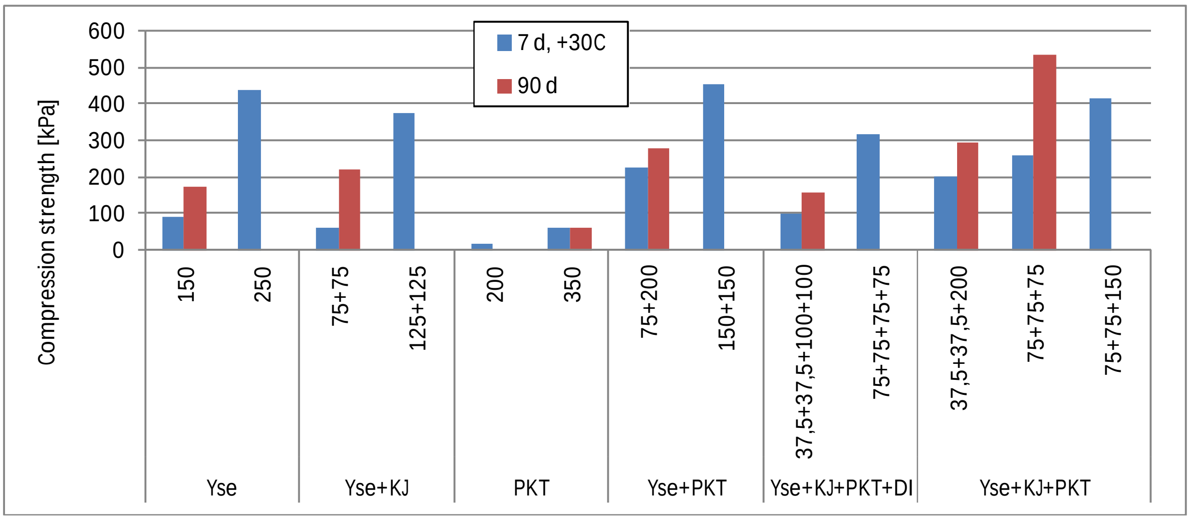

Figure 20. Compression strength results for sediment from Port of Gdynia

Oil shale ash is not working as only binder component if 100-200 kPa of compression strength is needed. Mixture of cement and oil shale ash is working well; oil shale ash can substitute considerable amount of cement. For example same compression strength can be obtained after 7 days of curing time in +30 ºC by using either 250 kg/m^3 of cement or 150 kg/m^3 of cement + 150 kg/m^3 of oil shale ash.

Mixture of cement-blast furnace slag and oil shale ash is working well. For example 260 kPa compression strength after 7 days of curing time in +30 ºC can be obtained by Yse+KJ+PKT mixture of

75+75+75 kg/m^3 or by Yse+KJ mixture of approximately 110 +110 kg/m^3. Increasing of the amount of oil shale ash in Yse+KJ+PKT mixture increases the compression strength value.

Substituting the amount of oil shale ash with gypsum does not give extra strength to the mixture but it reduces the strength as it can be seen from results; Yse+KJ+PKT 75+75+150 kg/m^3 and Yse+KJ+PKT+DI 75+75+75+75 kg/m^3.

10. SUMMARY OF TECHNICAL PART

West Harbour in Helsinki (Jätkäsaari)
- The sediment material is easily strengthened with low binder amount
- High compression strength values can be obtained by using oil shale ash as only binder component. There are differences between oil shale ash qualities: electric filter ash from new burning technology, electric filter ash from old burning technology and cyclone ash from old burning technology are listed in series with decreasing compression strength obtained.
- Already low amount of cement (20 kg/m^3) combined with oil shale ash give high compression strength values. The differences between compression strength results of oil shale ash qualities combined with constant cement amount are fairly small.
- Gypsum does not bring extra benefit to strength when combined with cement and oil shale ash.

Fairway of Kokkola
- Proper compression strength values are not obtained when oil shale ash is used as only binder component. Oil shale ash qualities tested are cyclone ash, electric filter ash and bottom ash
- When oil shale ash is combined with cement, good compression strength values are obtained especially when the amount of oil shale ash is increased in the mixture. All tested oil shale ash qualities give proper strength when combined with cement if the amount of oil shale ash is sufficient.
- Gypsum does not bring extra benefit to strength when combined with cement and oil shale ash.

Port of Kokkola, Deep Port
- Good compression strength values can be obtained by using oil shale ash as only binder component.
- With small addition of cement (20-30 kg/m^3) to oil shale ash, compression strength can be increased considerably.
- Gypsum does not bring extra benefit to strength when combined with cement and oil shale ash.
- Long-term strength development is remarkable for oil shale ash and cement-oil shale ash mixture. Strength development continues for a year.

River Kymi
- The water content and organic matter content of sediment is high and as a result higher binder amounts are needed than for other sediments tested
- Proper compression strength values are not obtained when oil shale ash is used as only binder component.
- When oil shale ash is combined with cement, good compression strength values are obtained but the amount of cement has to be quite high (approx. 100 kg/m^3) in the mixture.
- Depart from other sediments tested gypsum brings extra benefit to strength when combined with cement and oil shale ash.

Port of Klaipeda
- Proper compression strength values are not obtained when oil shale ash is used as only binder component.
- The amount of cement was too low in tested cement-oil shale ash mixtures and as a result the compression strength values were low. Probably the compression strength values would have been good when the amount of cement would have been about 100 kg/m^3 in the cement-oil shale ash mixtures.
- The effect of water content of sediment on strength was obvious; with constant amount of cement-oil shale ash mixture the compression strength for drier sediment sample was clearly higher.

Gdynia
- Proper compression strength values are not obtained when oil shale ash is used as only binder component.
- When oil shale ash is combined with cement, good compression strength values are obtained

- When oil shale ash is combined with cement and blast furnace slag equal compression strength can be obtained as when combined with cement
- Gypsum does not bring extra benefit to strength when combined with cement-blast furnace slag and oil shale ash

11. CHEMICAL FINDINGS

The effectiveness of gypsum in environmentally sustainable sediment stabilization was evaluated with different sediment matrices. Considered sediment matrices were from Port of Kokkola, river Kymijoki, and Port of Gävle. Basic cement from Finland (Yse) and from Sweden (Byggcement), Merit slag, fly ash from Alholmens Kraft in Pietarsaari, oil shale ash from Eesti Energia Narva plant, and dihydrate gypsum from Yara Suomi in Siilinjärvi were investigated as binders. Some key findings are presented here, but for more detailed information the reader is directed to analytical results report of SMOCS published in LUT series.

11.1 Leaching results

Table 13 shows the leaching from binder materials and sediments without stabilization. In Kymijoki sediment, the main contaminant is mercury that exceeds limit value for non-hazardous waste. In Port of Kokkola sediment, zinc is considered as the most significant contaminant, but also nickel is leaching beyond the limit for inert waste. In Port of Gävle sediment, leaching of mercury, arsenic, and chloride is noticeable. Leaching of sulphate exists in all samples and binder materials. Chromium is found in both cement grades as well as in both ashes.

Table 13 Cumulative leaching concentrations of binder materials and sediment samples (Kymijoki, Gävle, Kokkola) from 2-stage batch test. Values exceeding limit values for leaching of inert waste, non-hazardous waste and hazardous waste are shown (bold, double border and grey background).

[mg/kg]	Kymijoki	Gävle	Kokkola	Yse (cement)	Byggcement	Merit (slag)	LT (fly ash)	PKT (oil shale ash)	DI (gypsum)
Hg	0.27	0.02	0.01	0.01	0.00	0.00	0.00	0.00	0.00
As	0.00	0.58	0.02	0.00	0.00	0.00	0.00	0.00	0.00
Ca	173.27	272.54	232.57	6216.60	5413.67	1068.06	5523.23	9980.47	5990.55
Cr	0.00	0.00	0.20	6.21	1.06	0.01	7.42	1.23	0.00
Cu	0.00	0.00	1.58	0.00	0.00	0.00	0.00	0.00	0.22
Fe	1.83	0.28	1.36	1.37	0.25	0.96	1.05	0.27	0.62
Mg	47.82	450.50	123.97	0.18	0.13	0.49	0.52	0.25	18.54
Mn	3.83	0.90	0.00	0.00	0.00	0.00	0.00	0.00	10.46
Mo	0.00	0.50	0.01	1.23	0.09	0.00	5.37	0.50	0.00
Ni	0.00	0.00	1.24	0.00	0.00	0.00	0.00	0.00	0.00
Se	0.00	0.00	0.00	0.01	0.01	0.00	0.15	0.00	0.00
Zn	0.38	0.00	41.95	0.00	0.00	0.00	0.02	0.00	0.42
SO4	1975.57	2496.41	5448.65	10599.44	9547.94	1342.39	42886.08	37979.54	80523.52
Cl	38.19	8977.45	885.65	121.79	53.58	15.43	1999.29	1222.67	24.21

Figures 21-24 illustrate the leaching from stabilized samples. Figure 21 shows the results from Port of Kokkola case. The sediment sample is stabilized with a mixture of cement, gypsum, and oil shale ash with amounts of 0 kg/m^3 or 100 kg/m^3. Cement is constant 50 kg/m^3 in each case. For example, the leaching of zinc can be minimized with a mixture of cement (50 kg/m^3), gypsum (100 kg/m^3) and oil shale ash (100 kg/m^3). Bu using oil shale ash or gypsum alone with cement will lead to roughly the same leaching amount ~0.15 mg/kg$_{dw.}$. However, in the sample stabilized with the mixture of all the binders, the leaching is only 0.01 mg/kg$_{dw}$.

In Figure 22, for instance, the leaching of chromium can be seen in case river Kymijoki. The addition of oil shale ash increases the leaching of chromium and in the mixture of cement (100 kg/m^3), oil shale ash (100 kg/m^3) and gypsum (100 kg/m^3) the leaching is even higher. In other sediment matrices this behavior was not seen, i.e. the amounts were below detection limit. The Kymijoki sediment differs from other cases due to its high organic content.

Figures 23 and 24 illustrate case Port of Gävle, where in addition slag (KJ) was investigated. The constant amount of cement was 50 kg/m^3 in this case. The most interesting finding is the origin of nickel leaching that seems to be the cement.

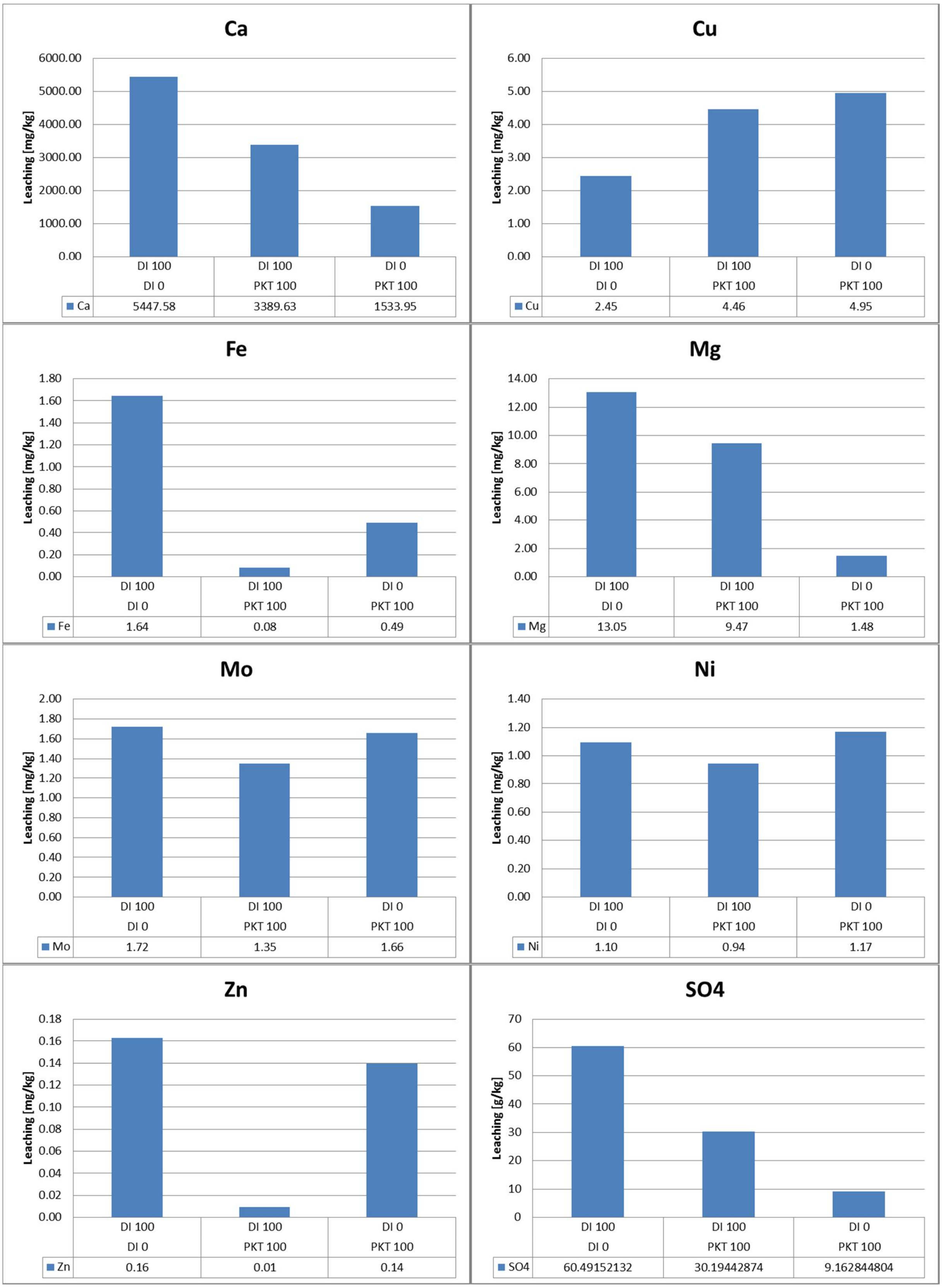

Figure 21 Illustration of influence of binder materials on cumulative leaching of some key contaminants in Port of Kokkola sediment. All mixtures include cement Yse 50 kg/m^3.

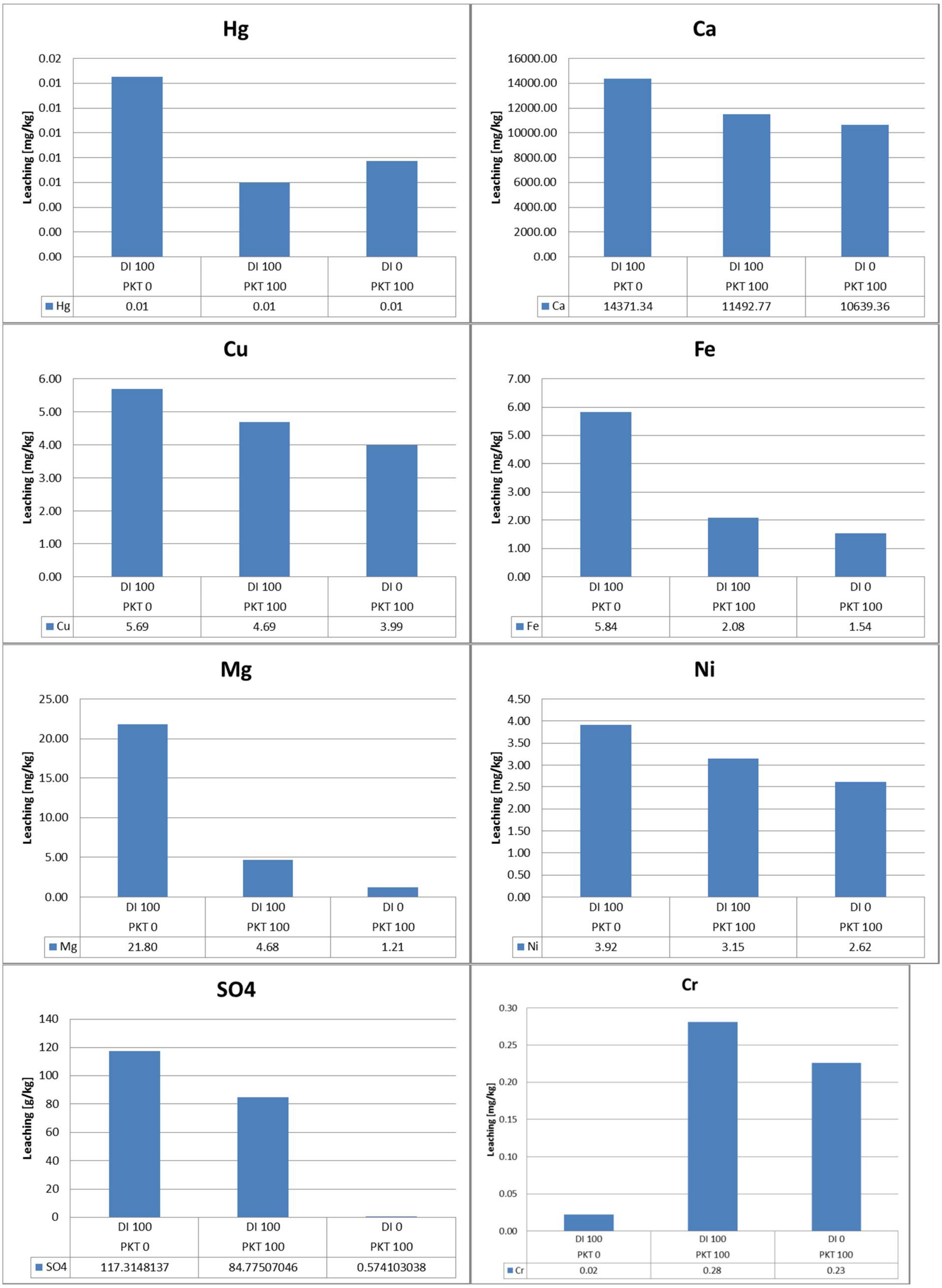

Figure 22 Illustration of influence of binder materials on cumulative leaching of some key contaminants in river Kymijoki sediment. All mixtures include cement Yse 100 kg/m^3.

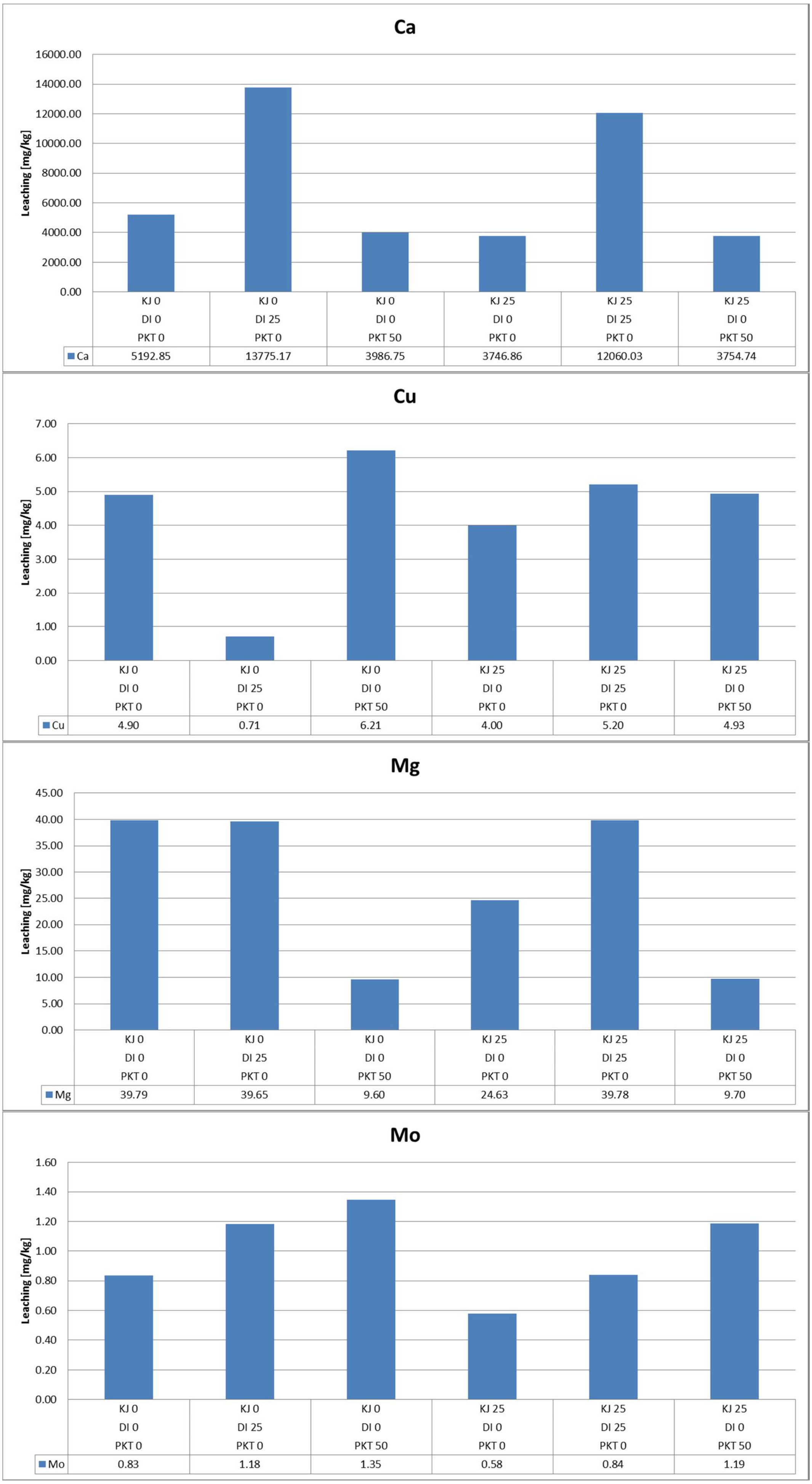

Figure 23 Illustration of influence of binder materials on cumulative leaching of some key contaminants in Port of Gävle. All mixtures include cement Byggcement 50 kg/m^3.

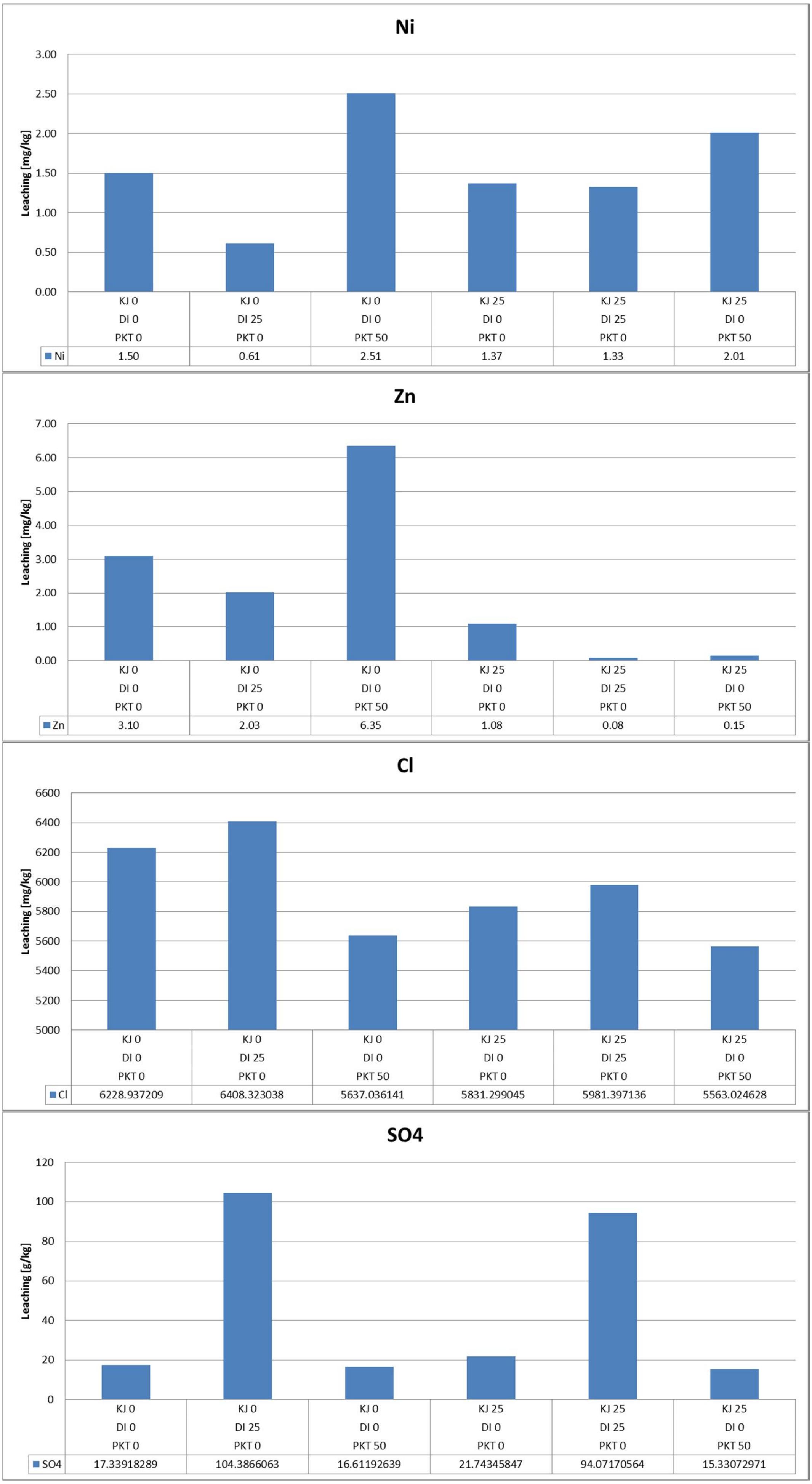

Figure 24 Illustration of influence of binder materials on cumulative leaching of some key contaminants in Port of Gävle. All mixtures include cement Byggcement 50 kg/m^3.

11.2 Leaching dynamics

The leaching dynamics was investigated by a modified approach to 2-stage batch test. Subsamples were taken at different time intervals. At each sampling step, the leachate volume was kept constant and the change in concentration was taken into account in calculations. The measured concentrations were used in calculation of cumulative leaching of each element. Figures 25 and 26 show the trend in leaching with a few mixtures. The samples are made with Port of Kokkola sediment. For instance, it can be seen that the addition of either gypsum or oil shale ash will reduce significantly the leaching of zinc. As the leaching time grows, the leaching trend seems to diminish indicating that the bioavailability reduces. With several elements the trend levels after some time, but with some elements a slightly increasing trend is still visible after 48 hours. However, the first hours seem to be dominant.

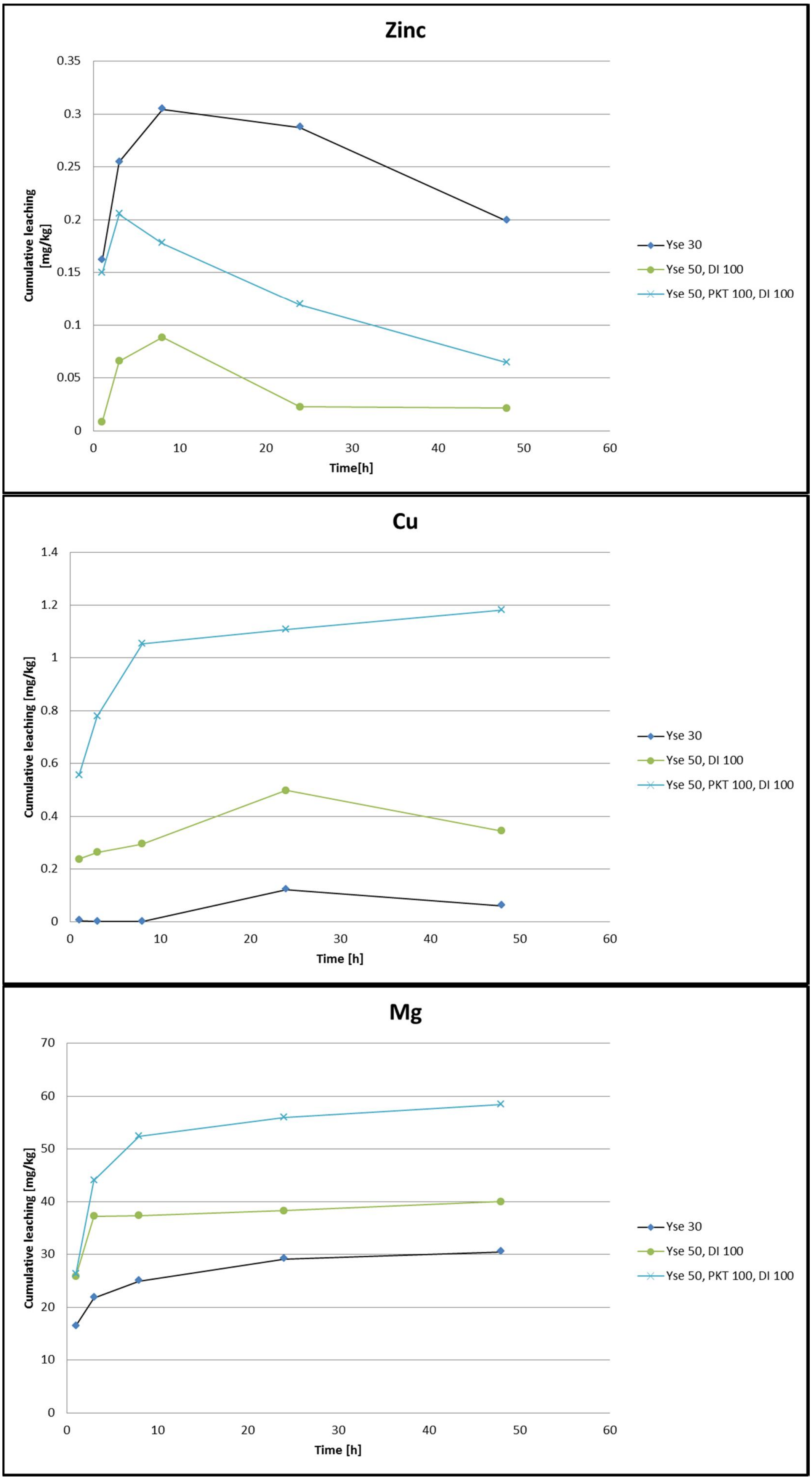

Figure 25 Time dependence of cumulative leaching with various binder mixture combinations. Sediment matrix from Port of Kokkola

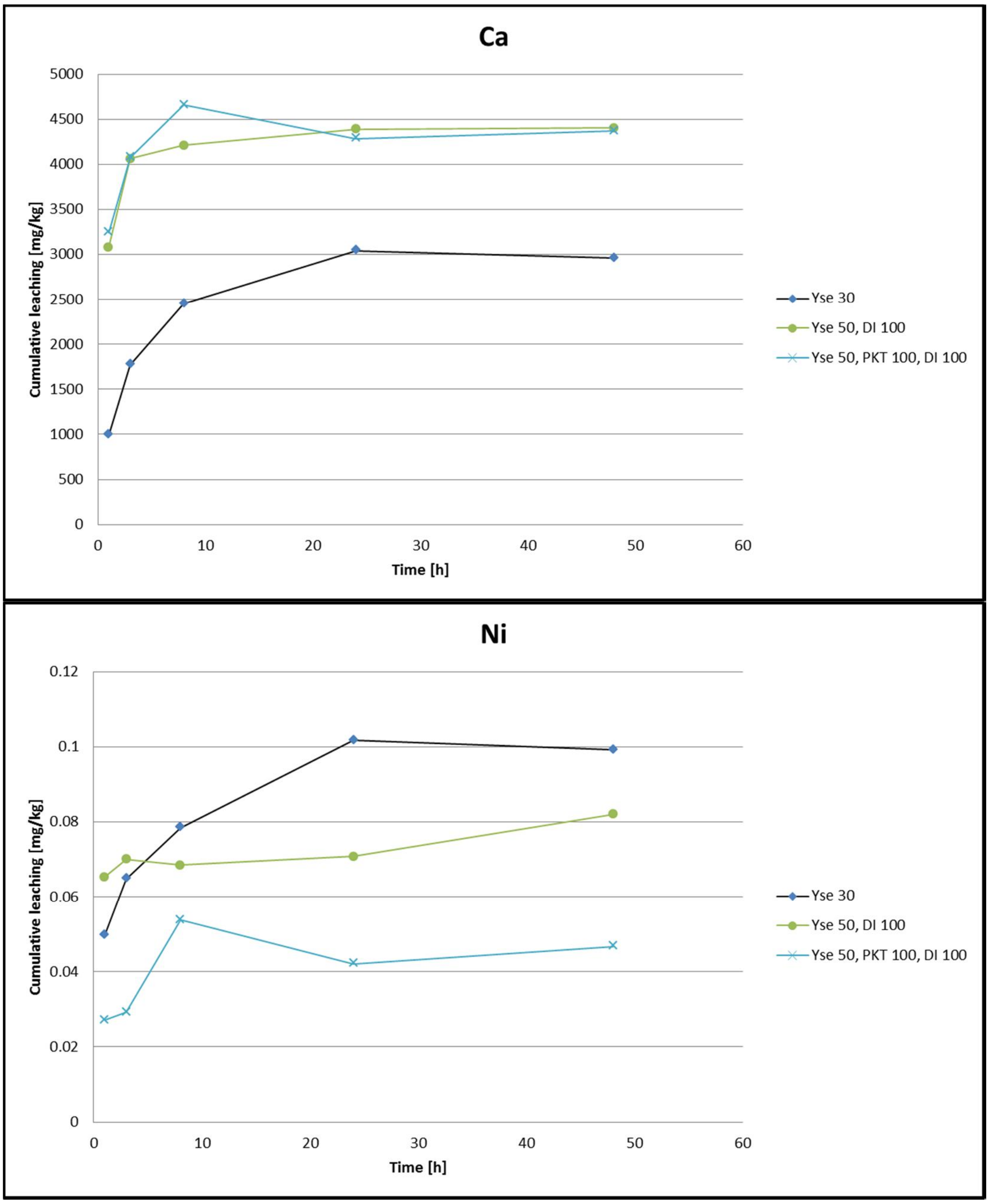

Figure 26 Time dependence of cumulative leaching with various binder mixture combinations. Sediment matrix from Port of Kokkola

11.3 SEM imaging

Scanning electron microscopy (SEM) imaging was used to visualize samples stabilized with different binder compositions. In Figure 27, gypsum is visualized and in Figure 28, a sample stabilized with a mixture of cement and gypsum is shown.

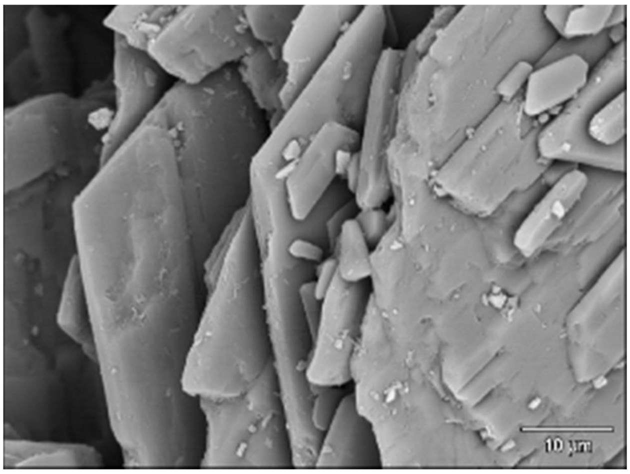

Figure 27 Gypsum sample

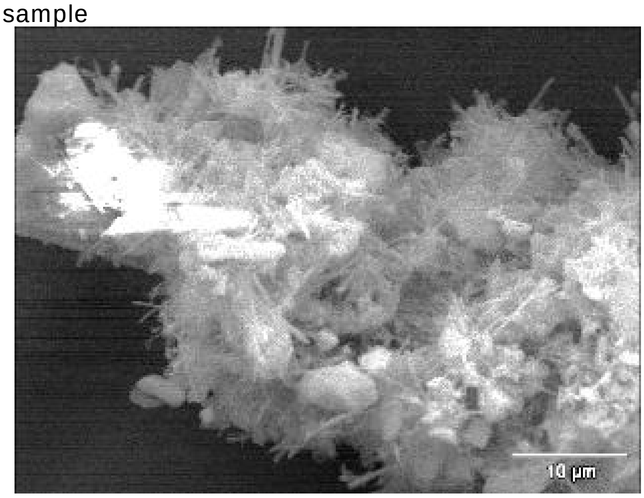

Figure 28 Cement and gypsum 100 + 200 kg/m^3 (Kymijoki)

Figure 29 shows a sample from river Kymijoki stabilized with oil shale ash. Figures 30 and 31 show samples from Kymijoki or Port of Kokkola stabilized with mixtures of cement and oil shale ash. More images can be found in the analytical report of SMOCS published in LUT series.

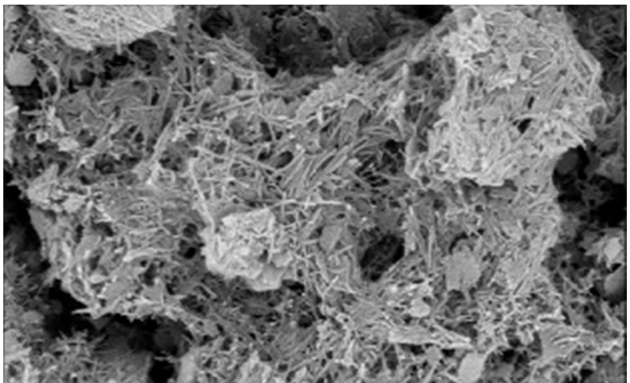

Figure 29 Kymijoki sample and oil shale ash 300 kg/m^3 after one month curing period.

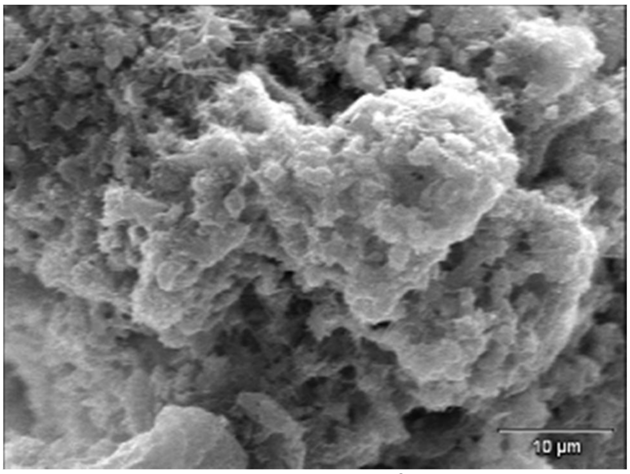

Figure 30 Cement and oil shale ash 100 + 200 kg/m^3 (Kymijoki)

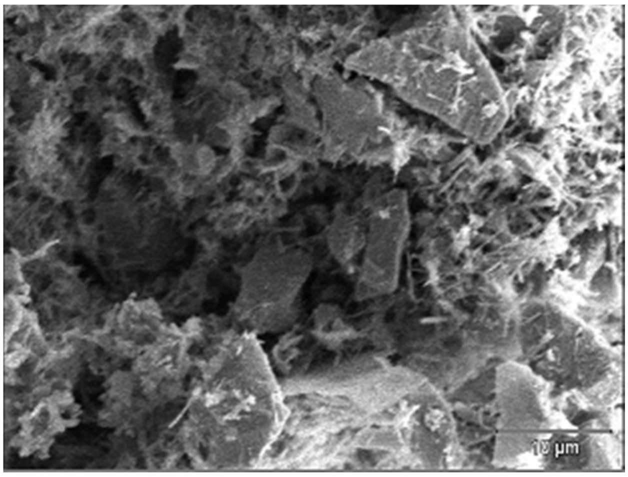

Figure 31 Cement and oil shale ash 40 + 150 kg/m^3 (Port of Kokkola)

12. CONCLUSIONS

Oil shale ash qualities are very potential binders for stabilisation of sediments. Especially electron filter and cyclone fly ashes are working well. For many sediments tested in this study oil shale ash is not working as only binder component, but cement activation is needed if target compression strength is about 100-200 kPa. Exceptions for this are sediments from West Harbour in Helsinki and sediments from Deep Port from Kokkola for which good compression strength values were obtained by using only oil shale ash.

Good compression strength values are obtained when oil shale ash is combined with cement. However, if water content or organic matter content of sediment is high, the amount of cement needed is quite high. In any case by using of oil shale ash the demand of cement and other commercial binders are reduced considerably. That saves binder costs.

In most cases cement-oil shale ash mixtures are working better than cement-oil shale ash-gypsum mixtures. It means that higher compression strength can be obtained by increasing the amount of oil shale ash in cement-oil shale ash mixture than substituting oil shale ash with gypsum. Exception for this is sediment from River Kymi were addition of gypsum was beneficial for strength.

The effect of oil shale ash quality on strength is obvious, but the best oil shale ash quality has to be tested case by case.

1. APPENDIX 1

WEST HARBOUR IN HELSINKI, JÄTKÄSAARI

Binder	Amount of binder [kg/m³]	Compression strength [kPa]		
		28 d	90 d	14 d at +30ºC
PKT(A)	50	31	45	
	100	128	155	
	150	249	305	590
	200	367	790	
Yse+PKT(A)	20+100	260	401	515
	30+50	179	262	
	30+100	303	527	689
	30+150	430	763	
	50+50	311	406	581
	50+100	395	677	
Yse+PKT(A)+kipsi	30+50+50	237	339	458
	30+67+33	305	499	644
	30+100+50	340	678	
	50+30+20	359	483	625
	50+50+50	362	618	
	50+70+30	421	734	
PKT (B)	50	9	13	
	150	316	422	524
Yse+PKT(B)	30+100	370	484	714
	50+50	305	385	
Yse+PKT(B)+kipsi	30+67+33	285	371	419
	50+50+50	409	532	
PKT (C)	50	39	35	
	150	122	171	359
Yse+PKT(C)	30+100	286	460	
	50+50	309	433	
Yse+PKT(C)+kipsi	30+67+33	332	527	
	50+50+50	341	600	

PKT(A) = filter ash/I-field, old burning technology. EPP.

PKT(B) = filter ash/II-field, new burning technology. EPP.

PKT `(C) = cyclone ash, old burning technology. EPP.

FAIRWAY OF KOKKOLA

Stabilisation tests: Stage 1

Sample Point	Binder(s)	Amount [kg/m^3]	Compression strenght [kPa] 7 d/+30ºC	14 d/+30ºC
KS219 0-50cm	OSA C	100		2
		125		3
		150		3
		175		5
		200		6
		250		7
		300	18	
	Cem.+ OSA C	30+150	15	
		50+150	29	
	Cem.+ OSA C+ Gyp.	150+150		6
		50+100+100	92	
		40+100+100	42	
		30+100+100	14	
		30+150+150	18	
		20+100+100		13
	Cem.+ FA + OSA C + Gyp.	30+100+50+100	15	
		30+100+100+100	25	

Stabilisation tests: Stage 2

Sample Point	Binder: Binder(s)	Binder: Amount [kg/m³]	Compression strenght [kPa]: 28 d/30°C	Compression strenght [kPa]: 90 d
KS219 0-50cm	OSA C	300	30	34
	OSA BA	300	27	68
	OSA EF	300	7	14
	Cem.+OSA C	30+150	31	90
		30+200	72	147
		30+250	144	177
		30+300	234	230
	Cem.+ OSA BA	30+150	162	114
	Cem.+ OSA EF	30+150	126	55
	Cem.+OSA C+ Gyp.	30+150+150	335	179
		30+100+150	373	147
		30+150+100	276	147
	Cem.+ OSA BA+ Gyp.	30+150+150	144	108
	Cem.+ OSA EF+ Gyp.	30+150+150	138	196
	Cem.+ FA+ OSA C+ Gyp.	30+200+100+100	499	334

FAIRWAY OF KOKKOLA

Stabilisation tests: Stage 3

Sample Point	Binder: Binder(s)	Binder: Amount [kg/m³]	Compression strenght [kPa]: 28 d/+30°C	Compression strenght [kPa]: 28 d
KS201 0-50cm	Cem.+ OSA C+ Gyp	30+150+150	81	54
	Cem.+ OSA BA	30+200	118	40
	Cem.+FA+ OSA C+Gyp	30+200+100+100	305	114
KS213 0-50cm	Cem.+ OSA C+ Gyp	30+150+150	250	44
	Cem.+ OSA BA	30+200	109	19
	Cem.+ OSA EF	30+300	777	2
	Cem.+FA+ OSA C+Gyp	30+200+100+100	401	66
		30+150+50+50	127	35
KS223 0-50cm	Cem.+ OSA C+ Gyp	30+150+150	103	8
	Cem.+ OSA BA	30+200	49	6
	Cem.+FA+ OSA C+Gyp	30+200+100+100	362	29

PORT OF KOKKOLA, DEEP PORT

Binder amount [kg/m³]	Base material	Compression strength [kPa]	
		28 d	90 d
Yse + PKT 30+100	KS201+KS202, w_0	89	140
Yse + PKT 30 + 200	KS201+KS202, w_0	179	
Yse + PKT + DI 30 + 50 + 50	KS201+KS202, w_0	34	182
Yse + PKT + DI 30 + 100 + 100	KS201+KS202, w_0	84	270
Yse + KJ + PKT 15 + 30 + 100	KS201+KS202, w_0	53	61
Yse + KJ + PKT 15 + 30 + 200	KS201+KS202, w_0	74	385
Yse + KJ + PKT + DI 15 + 30 + 50 + 50	KS201+KS202, w_0	20	224
Yse + KJ + PKT + DI 15+30+100 + 100	KS201+KS202, w_0	32	121
PKT + DI 50 + 50	KS201+KS202, w_0	12	
PKT + DI 100 + 100	KS201+KS202, w_0	14	
KJ + PKT 60 + 100	KS201+KS202, w_0	19	20
KJ + PKT 60 + 200	KS201+KS202, w_0	35	190
KJ + PKT + DI 60 + 50 + 50	KS201+KS202, w_0	16	113
KJ + PKT + DI 60 + 100 + 100	KS201+KS202, w_0	17	34

Binder amount [kg/m³]	Base material	Compression strength [kPa]		
		7 d, +30°C	28 d,+ 30 °C	90 d
Yse + PKT 70 + 150	KS201, w_0	50	351	463
Yse + PKT 50 + 150	KS201, w_0	46	295	395
Yse + PKT 30 + 150	KS201, w_0	34	182	278
GTC + PKT 70 + 150	KS201, w_0	27	177	131
GTC + PKT 70 + 150	KS201, w_0	29	138	92
Yse + PKT + kipsi 70+75+75	KS201, w_0	35	584	321
Yse + PKT + kipsi 50+100+100	KS201, w_0	26	107	247
Yse + PKT + kipsi 30 + 100+ 100	KS201, w_0	23	79	208
(YSe+K400)+PKT+kipsi 70+75+75	KS201, w_0	31	141	424
(Yse+K400)+PKT 70+150	KS201, w_0	43	203	336

PORT OF KOKKOLA, DEEP PORT

Binder amount [kg/m3]	Base material	Compression strength [kPa]				
		28 d, +30°C	28 d	90 d	180 d	365 d
PKT 150	KS201, w_0	124	32	101		
PKT 200	KS201, w_0	165	37	150	360	532
PKT 300	KS201, w_0	1067	95	738		
Yse + PKT 40 + 150	KS201, w_0	182	126	288	422	512
Yse + PKT 30 + 150	KS201, w_0	251	67	249		
PeSe + PKT 30 + 150	KS201, w_0	237	80	284		
Pika + PKT 30 + 150	KS201, w_0	290	220	318		
Yse + PKT 20 + 150	KS201, w_0	187	44	171		
Pika + PKT 20 + 150	KS201, w_0	238	100	235		
Yse + PKT 20 + 200	KS201, w_0	351	73	335		
Yse + PKT 10 + 150	KS201, w_0	155	45	119		
Yse + PKT 10 + 200	KS201, w_0	292	96	224		
Yse + PKT + kipsi 50+100+100	KS201, w_0	279	100	282	348	334
PeSe + PKT + kipsi 50+100+100	KS201, w_0	639	106	528		
Pika + PKT + kipsi 50+100+100	KS201, w_0	774	163	499		
Yse + PKT + kipsi 50+150+100	KS201, w_0	1142	138	577		
Yse + PKT + kipsi 50+100+150	KS201, w_0	759	149	486		
Yse + PKT + kipsi 40+150+100	KS201, w_0	950	111	458		
Yse + PKT + kipsi 40+200+100	KS201, w_0	1310	137	554		
Yse + PKT + kipsi 40+100+150	KS201, w_0	512	94	397		
Yse + PKT + kipsi 40+100+200	KS201, w_0	607	88	391		
Yse + PKT + kipsi 40+150+150	KS201, w_0	947	115	488		
Yse + PKT + kipsi 30+150+150	KS201, w_0	668	103	390		

RIVER KYMI

Binders	Amount of binders [kg/m³]				Compression strength [kPa]	
	Binder 1	Binder 2	Binder 3	Binder 4	7 d at +30°C	90 d
Yse	200				61	126
	300				206	
Yse+KJ	100	100			38	143
PKT	300				10	13
Yse+PKT	150	200			268	411
	150	200			254	
	200	100			220	
Yse+KJ+PKT+DI	75	75	100	100	<10	265
	75	75	100	100	<10	
	100	100	50	50	<10	614
Yse+KJ+PKT	75	75	100		25	212/ 240*
	75	75	200		138	
	100	100	100		81	490

* Estimation at the age of 90 d is 240 kPa, 212 kPa is tested at the age of 65 d

Base material (sediment)	Binder(s) Quality	Quantity [kg/m3]	1-axial compression strength [kPa] thermal treatment (+30ºC) 4-6 d	thermal treatment (+30ºC) 28 d	normal treatment (+8ºC) 90 d
Aggregate sample nr 1 + nr 2	PKT ef	250	<10 (6 d)	<10	<10
	PKT ef	350	<10 (6 d)	<10	<10
	PKT ef	450	<10 (5 d)	<10	<10
	Yleis	100	8 (5 d)	14	15
	Yleis	150	20 (5 d)	104	46
	Yleis	200	64 (5 d)	215	192
	PKT ef+Yleis	200+30	<10 (5 d)	102	<10
	PKT ef+Yleis	200+50	<10 (4 d)	272	25
	PKT ef+Yleis	200+75	7 (4 d)	494	61
	PKTef+Yleis+KI	100+30+100	<10 (4 d)	<10	<10
	PKTef+Yleis+KI	150+50+150	<10 (4 d)	269	7
	PKT c	350	<10 (3 d)	11	5
	PKT c+Yleis	200+50	<10 (3 d)	22	26
	PKT ba	350	<10 (3 d)	<10	<10
	PKT ba+Yleis	200+50	<10 (4 d)	52	24
Aggregate sample nr 5 + nr 6	PKT ef	250	<10 (5 d)	<10	<10
	PKT ef	350	<10 (5 d)	<10	<10
	PKT ef	450	<10 (5 d)	<10	<10
	Yleis	100	11 (5 d)	18	13
	Yleis	150	30 (5 d)	77	53
	Yleis	200	79 (5 d)	316	201
	PKT ef+Yleis	200+30	<10 (5 d)	116	<10
	PKT ef+Yleis	200+50	<10 (5 d)	344	26
	PKT ef+Yleis	200+75	18 (5 d)	484	88
	PKTef+Yleis+KI	100+30+100	<10 (5 d)	<10	<10
	PKTef+Yleis+KI	150+50+150	<10 (5 d)	37	6
	PKT c	350	<10 (4 d)	22	6
	PKT c+Yleis	200+50	24 (5 d)	30	30
	PKT ba	350	<10 (4 d)	<10	<10
	PKT ba+Yleis	200+50	<10 (4 d)	55	21
Sample T3	PKT ef	350	<10 (4 d)	<10	<10
	Yleis	150	35 (5 d)	81	58
	PKT ef+Yleis	200+50	<10 (4 d)	380	12
Sample nr4	PKT ef	350	<10 (4 d)	9	<10
	Yleis	150	171 (5 d)	322	318
	PKT ef+Yleis	200+50	51 (5 d)	584	100

PORT OF GDYNIA

Binders	Amount of binders [kg/m³]				Compression strength [kPa]	
	Binder 1	Binder 2	Binder 3	Binder 4	7 d, +30 ºC	90 d
Yse	150				91	172
	250				436	
Yse+KJ	75	75			59	220
	125	125			375	
PKT	200				16	
	350				60	63
Yse+PKT	75	200			227	280
	150	150			452	
Yse+KJ+PKT+DI	37,5	37,5	100	100	98	156
	75	75	75	75	292	
	75	75	75	75	338	
Yse+KJ+PKT	37,5	37,5	200		200	294
	75	75	75		261	533
	75	75	150		415	

Appendix 3

Intended for
Yara Suomi Oy

Document type
Research report

Date
12.10.2012

STABILISATION OF SEDIMENT BY USING GYPSUM AS BINDER YARA SUOMI OY

RAMBOLL

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Checked by	LUONNOS
Approved by	

Ref	82128370-06

CONTENTS

APPENDIX

1. INTRODUCTION

The purpose of the stabilization tests has been studying the potential of gypsum from Yara Suomi Oy as a binder material in stabilization of sediments. The sediment materials included in the studies are from West Harbor in Helsinki in Finland; from Port of Kokkola in Finland; from River Kymi in Finland; from Port of Klaipeda in Lithuania and from Port of Gdynia in Poland.

The studies have been carried out as part of the SMOCS project (Sustainable Management of Contaminated Sediments), in which the stabilization properties and effects of different binders on stabilization of Baltic Sea sediments have been studied amongst other things.

In this report following issues have been reported:

- Geotechnical index properties of sediment samples
- Strength development in an early stage
- Long term strength development
- Effect of water content of sediment on strength
- Optimization of binder recipes, i.e. quantity and quality of binders used

Stabilization studies in different cases have proceeded to different stages. In most cases only preliminary results (Gdynia, Klaipeda, River Kymi) are available from stabilization studies. In Port of Kokkola and Jätkäsaari the studies have proceeded further.

Binders used in the studies are different cement qualities, lime, blast furnace slag, oil shale ash qualities of Eesti Energia and gypsum from Yara Suomi Oy.

Stabilization studies have been performed in the laboratory of Environmental Geotechnics of Ramboll Luopioinen in Finland and chemical analyzes in Ramboll Analytics.

2. GYPSUM OF YARA SUOMI OY

Phosphate gypsum is a side product originating from phosphoric acid production. Phosphate gypsum is produced in Yara Siilinjärvi plant, where phosphoric acid is produced from apatite. Phosphate gypsum is produced as a side product approximately 1,6 million tons a year. When tricalcium phosphate reacts with sulphuric acid, phosphoric acid and dihydrate gypsum is formed.

Phosphate gypsum consists mainly of sulphate, calcium oxide, silicon oxide and crystal water. Even there are relatively few detrimental elements, the concentrations of phosphorus, fluoride and sulphide can cause problems. (kuva?) Optimum moisture percentage of phosphate gypsum is 15-20 % ja maximum dry density is 1470-1670 kg/m^3. Water permeability is 10^{-4}–10^{-5} m/s.

Total concentrations and leaching properties are shown in table 1. The results are compared to the limit values of utilization in earth construction limit values (Finnish Council of State’s regulation 403/2009 “the Council of State’s regulation of utilization of certain waste at earth construction to change the supplements 1 and 2”). The regulation doesn’t concern gypsum but as it concerns explicitly earth construction, the comparison gives a good understanding of gypsum’s usability in earth construction. Leaching properties of fluoride and sulphate exceeds the limit value for coated structure.

Leaching properties of fluoride and sulphate are according to validity of dumb pits 861/1997 (land fills) similar to ordinary waste which can be displaced in normal land fill (class B 1b).

Table 1. Total concentration and leaching properties of gypsum compared to earth construction limit values. Values of fluoride and sulphate exceeds the limit values.

	Kipsi			Perustutkimukset		
	Kokonais-pitoisuus [mg/kg ka]	Liukoisuus L/S 10 [mg/kg ka]	Liuenneen haitta-aineen osuus kokonaispitoisuudesta %	Kokonais-pitoisuus [mg/kg ka]	Peitetty rakenne Liukoisuus L/S 10 [mg/kg ka]	Päällystetty rakenne Liukoisuus L/S 10 [mg/kg ka]
Sb	<0,5	<0,020			0,06	0,18
As	17	<0,020		50	0,5	1,5
Ba	200	0,029	0,01 %	3 000	20	60
Hg	<0,2	<0,003			0,01	0,01
Cd	<0,2	<0,020		15	0,04	0,04
Cr	<1	<0,020		400	0,5	3
Cu	14	0,32	2,29 %	400	2	6
Pb	4,6	<0,020		300	0,5	1,5
Mo	<2	<0,020		50	0,5	6
Ni	<2	<0,020			0,4	1,2
Se	<1	0,024			0,1	0,5
Zn	<5	0,053		2 000	4	12
V	<1	<0,020		400	2	3
F^-		*64*			10	50
SO_4^{2-}		*13000*			1 000	10 000
Cl^-		<9,0			800	2 400
DOC		<11			500	500
TDS		22000				
pH-alku		5,2				
pH-loppu		4,7				

3. LABORATORY METHODS

Laboratory methods are shown in Appendix 2.

4. BINDERS

Binders are shown in Appendix 2.

5. WEST HARBOR IN HELSINKI, JÄTKÄSAARI

5.1 Materials

Sediment sampling was performed from the Saukonpaasi area in April 2010. Sampling from the Saukonpaasi area was performed by Suomen Vesityö Oy. Samples were taken with grab bucket.

The geotechnical index properties for sediment samples are shown in table 6. A combined sediment sample consisting of samples P4 1-2 m + P5 2-3 m + P5 4.5-5.5 m in proportion of 1:1:1 was used in stabilisation tests. The binders which were used in the study are shown in table 7.

Table 6. Geotechnical index properties of sediment samples from Jätkäsaari

Sample	w [%]	ρ_m [kg/m^3]	LoI [%]	pH
4 / 1-2 m	119	1410	4,2	8,0
5 / 2-3 m	111	1420	4,1	7,9
5 / 4,5-5,5 m	86	1510	3,6	8,2

Table 7. Binders used in stabilisation tests

Abbreviation	Name	Supplier	Other information
PKT A	oil shale ash	Eesti energia	filter ash/I-field, old burning technology. EPP
PKTB	oil shale ash	Eesti energia	filter ash/II-field, new burning technology. EPP
PKT C	oil shale ash	Eesti energia	cyclone ash, old burning technol-ogy. EPP
YSE	Ordinary Portland cement	Finnsementti	CEM II/A-M(S-LL) 42,5 N
kipsi, DI	gypsum	Yara Suomi Oy	Pile stored di-gypsum

5.2 Results

The results from 1-axial compression strength tests are shown in appendix 1. Gypsum was used together with oil shale ash and cement.
The sediment material can be stabilised with fairly low amount of binder: for example having 359 kPa compression strength after 28 days of curing time 50 kg/m^3 of cement + 30 kg/m^3 of oil shale ash + 20 kg/m^3 of gypsum is needed. With this binder mixture the compression strength was after 90 days 483 kPa. After 14 days thermal treatment the compression strength was as high as 625 kPa.

Compression strength results for cement-oil shale ash (A, B and C qualities)-gypsum mixtures are shown in figure 3. The thermal treatment tests show that the binder mixture has a potential for long-term strength development.

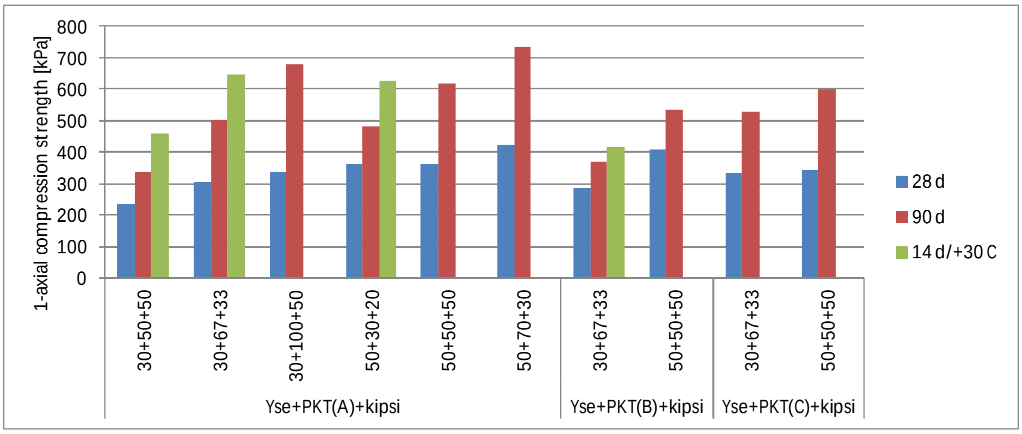

Figure 3. 1-axial compression strength results for cement-oil shale ash-gypsum mixtures (The units of the binder amounts are kg/m^3)

Comparison of cement-oil shale ash-gypsum mixtures and cement-oil shale ash mixtures are shown in figure 4. When the amount of cement is 50 kg/m^3 substitution of maximum 1/3 of the amount of oil shale ash with gypsum brings some extra strength to the mixture but if the amount of gypsum is higher the compression strength will decrease.

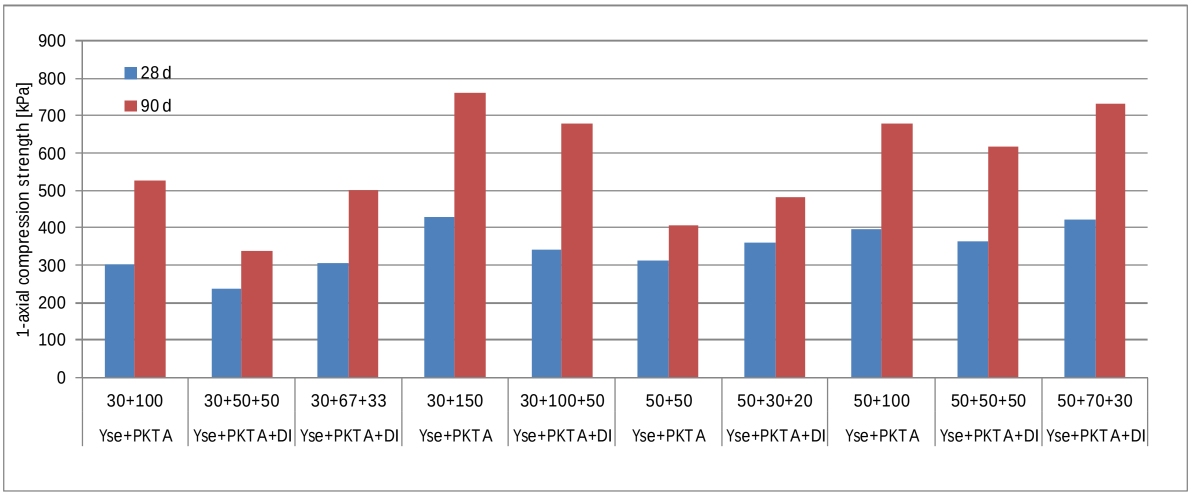

Figure 4. Comparison of cement-oil shale ash-gypsum mixtures and cement-oil shale ash mixtures (The units of the binder amounts are kg/m^3)

Compression strengths with different aggregate materials and gypsum and gypsum-fly ash –mixtures are shown in figure 8. When lime cement is combined with fly ash and gypsum, the results are quite the same as with only gypsum. When the aggregate material is dryer, the lime cement-gypsum –mixture works slightly better than lime cement-gypsum-fly ash –mixture.

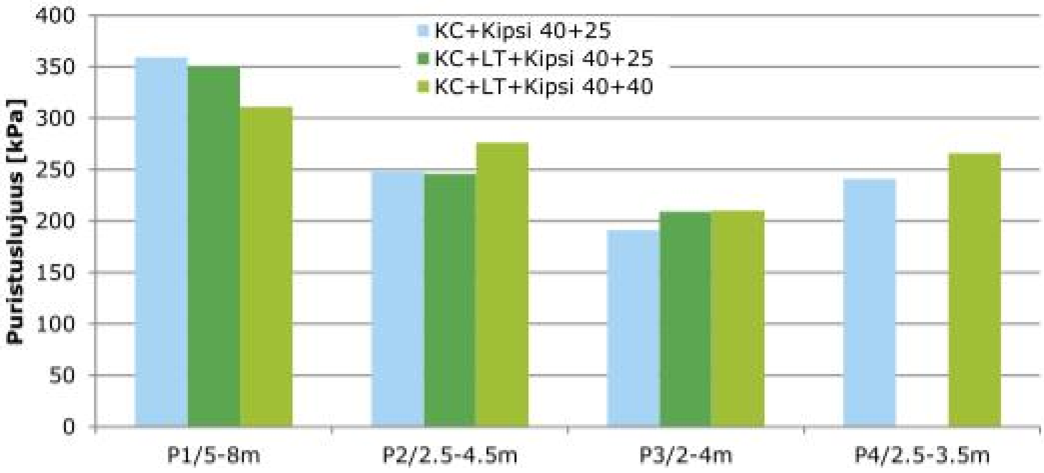

Figure 5. Differences in compression strengths with different aggregate material and gypsum and gypsum-fly ash –mixtures.

6. PORT OF KOKKOLA

Yara Suomi gypsum has been tested with sediments from Fairway of Kokkola and Kokkola Deep Port. Stabilization results from Fairway of Kokkola has been presented in report "Eesti Energia, Utilisation potential of oil shale ashes in the stabilisation of dredged sediments in the Port of Kokkola, Ramboll Finland Oy, 21.6.2011" and in chapter 5.2 is collected the most central results of that report.

6.1 Materials of Fairway of Kokkola

The stabilization tests were made for four (4) different sediment samples taken from the fairway of Kokkola. The characteristics of the sediments are represented in table 8.

Table 8. Sediment characteristics.

Sediment sample	water content [%]	Density ρ_m [kg/m^3]	Loss of ignition H_h [%]	Soil type
KS219 0-0,5m	153	1,34	3,7	muddy silt
KS213 0-0,5m	167	1,33	3,5	muddy silt
KS201 0-0,5m	52	1,71	1,5	silty loam
KS223 0-0,5m	120	1,42	2,1	silty loam

The stabilization tests were done with several different binder amounts and mixtures. The used binders were:

- gypsum, Gyp.
- oil shale cyclone ash, OSA C
- oil shale bottom ash, OSA BA
- oil shale electric filter ash, OSA EF
- Portland cement, Cem
- fly ash from combustion of mixed fuel (peat, wood, REF), FA

6.2 Results of Fairway of Kokkola

The stabilisation tests were done in three stages. The first two stages were done only with sample KS 219 0-50 cm and the last stage was done with three other sediment samples (KS 201, 213 and 223) to test the correspondence of the results with other sediment samples.

Gypsum was used in the stabilization tests together with cement and oil shale ash. The specimens were treated 28 days thermally (+30 °C) and normally (+8 °C). The results of the first stage are shown below in figure 5.

The thermal treatment results were good, but normal 28 d results were quite low in most cases.

Combination of oil shale ash with gypsum does not work. The results for combination of cement, oil shale ash and gypsum show that the amount of cement have to be sufficient (at least 50 kg/m^3) in order to achieve reasonable strength. Increasing the amounts of gypsum in the mixture does not bring benefit if the amount of cement is too low. Combination of four binder components, cement, fly ash, oil shale ash and gypsum, give low compression strength results with tested binder amounts.

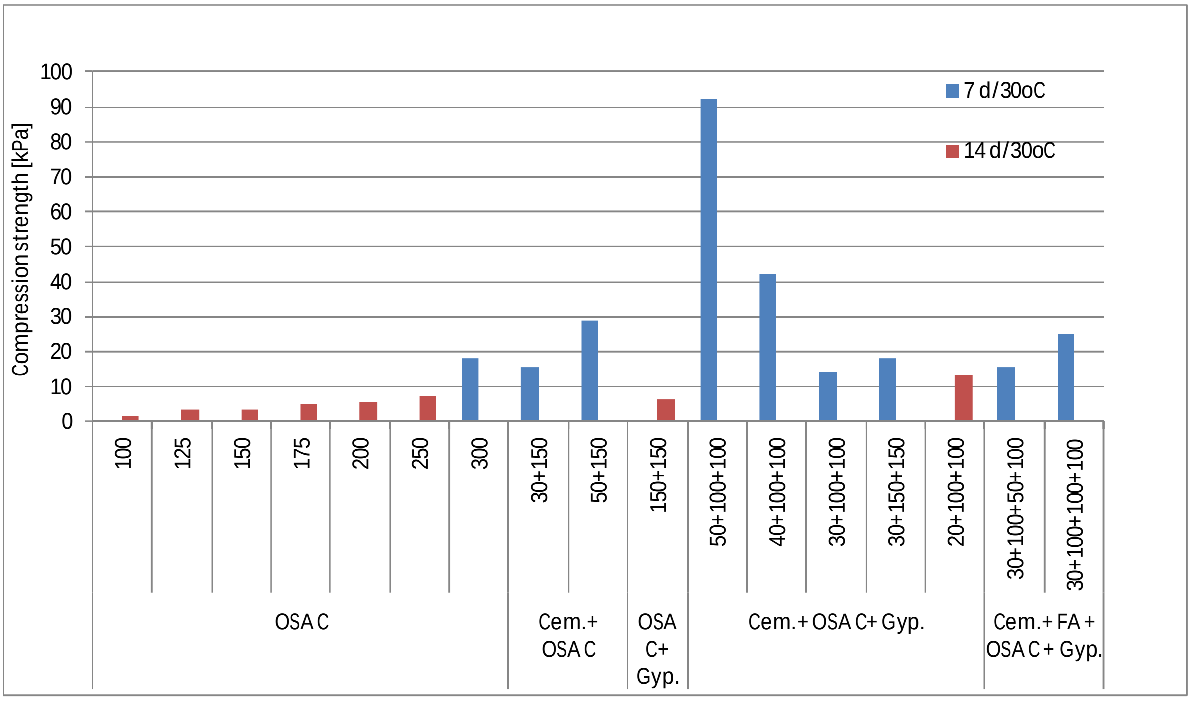

Figure 5. Results of the first stage stabilisation tests for KS 219 0-50 cm (The units of the binder amounts are kg/m^3)

On second stage every binder mixture were thermally treated for 28 days and normally treated for 90 days. The results of the second stage of the stabilization tests are shown in Figure 6 below.

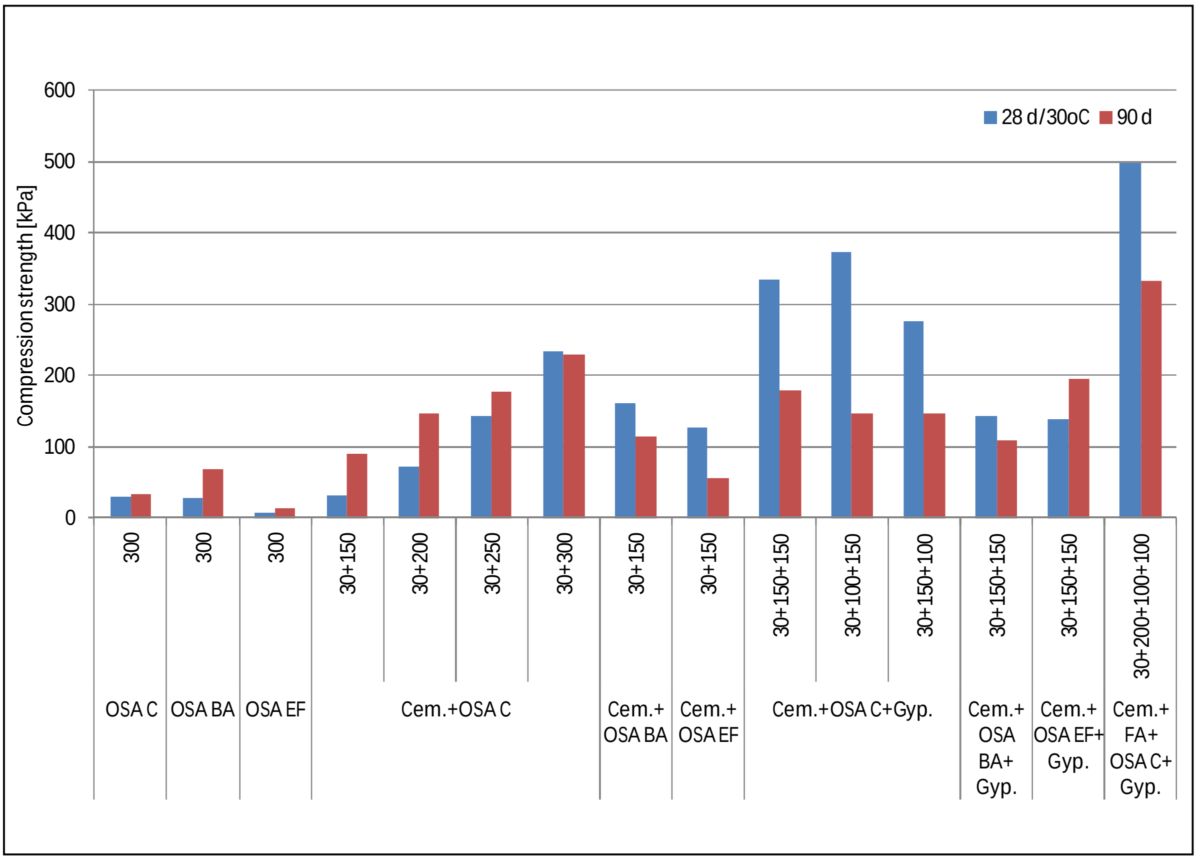

Figure 6. Results of the second stage of the stabilization tests for KS 219 0-50 cm (The units of the binder amounts are kg/m^3).

Results show that with combination of cement, fly ash, OSA C and gypsum the compression strength is high but the amount of binders is high as well. Thermal treatment gives conflicting results; most reliable comparisons between different binders can be made from results after 90 days of curing time in normal treatment at +8 ºC.

On the third stage the different binder mixtures were tested with three other samples. The different binder mixtures were thermally and normally treated for 28 days. The results of the third stage of the stabilization tests are shown below in Figure 7.

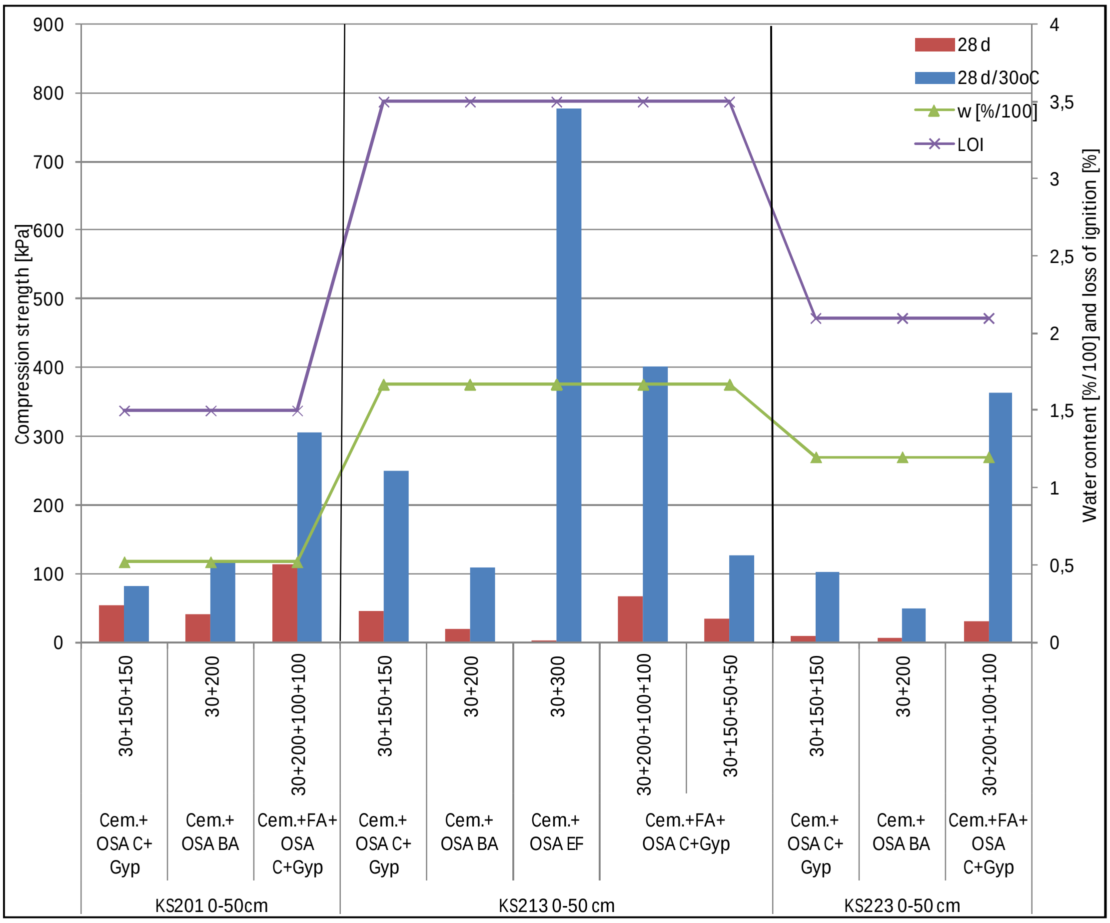

Figure 7. Results of the third stage of the stabilisation tests (The unit of the binder amounts is kg/m^3).

The figure 7 shows that according to the 28 d normally treated specimens the best compression strengths can be achieved with KS 201 0-50 cm, the second best results gave KS 213 0-50 cm and the lowest compression strengths gave the KS 223 0-50 cm sample. There is some consistency with water content and organic matter content of sediment samples with compression strength results; the sample with lowest water content and organic matter content had higher compression strength results than other samples with same binder combinations. Anyhow the sample with highest water content and organic matter content did not have lowest compression strength values. That is due to other differences between samples for example differences with grain size distribution or possible chemical contaminations in the samples, which can affect strength development.

6.3 Materials of Port of Kokkola, Deep port

The studied characterization tests were water content, density, loss of ignition, particle size distribution. The results are shown in table 8.

Table 8. Characterization of sediment samples.

Sample	w [%]	ρ_m [kg/m^3]	LoI [%]	Particle size
KS201+KS202	52	1700	1,3	silt
KS202	53	1700	1,2	silt
KS201	52	1700	1,5	silt

Binders used in stabilization were both commercial binders and industrial by-products. The used binders were

- Rapid Portland cement (Pika)
- Portland cement (YSe)
- Portland-Blast furnace slag cement (PeSe)
- Blast furnace slag (KJ)
- Gypsum (DI, kipsi)

- Oil shale ash, electric filter ash (PKT)

6.4 Results of Port of Kokkola, Deep port

6.4.1 Cement- gypsum mixtures

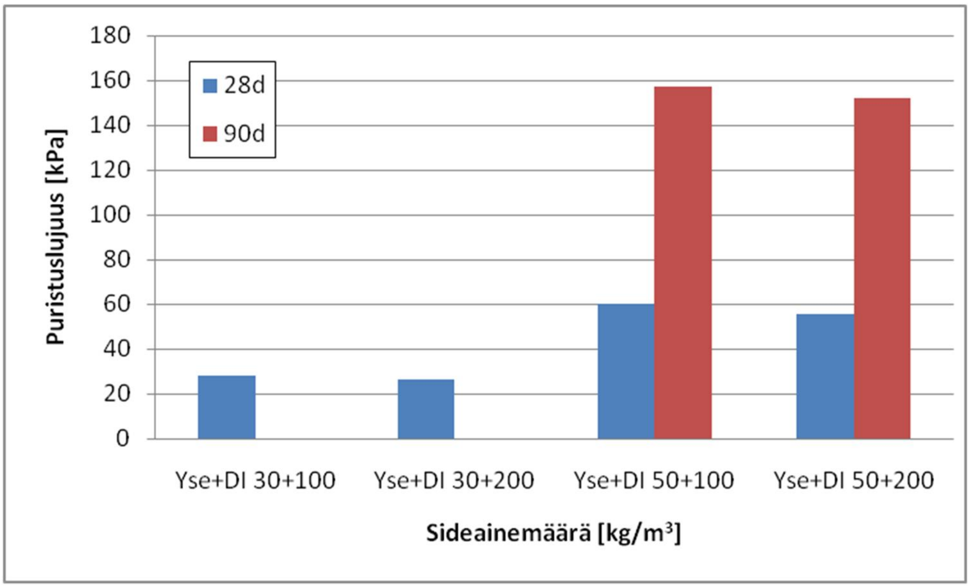

Figure 11. Functionality of cement-gypsum-mixture as a binder.

- 28 d compression strength results are low
- Time curing is significant as 90 d compression strengths are approximately 2,6 times as high as 28 d results
- Increasing the amount of gypsum from 100 kg/m3 to 200 kg/m3 doesn't have influence on strength results

6.4.2 Cement-fly ash-gypsum mixtures

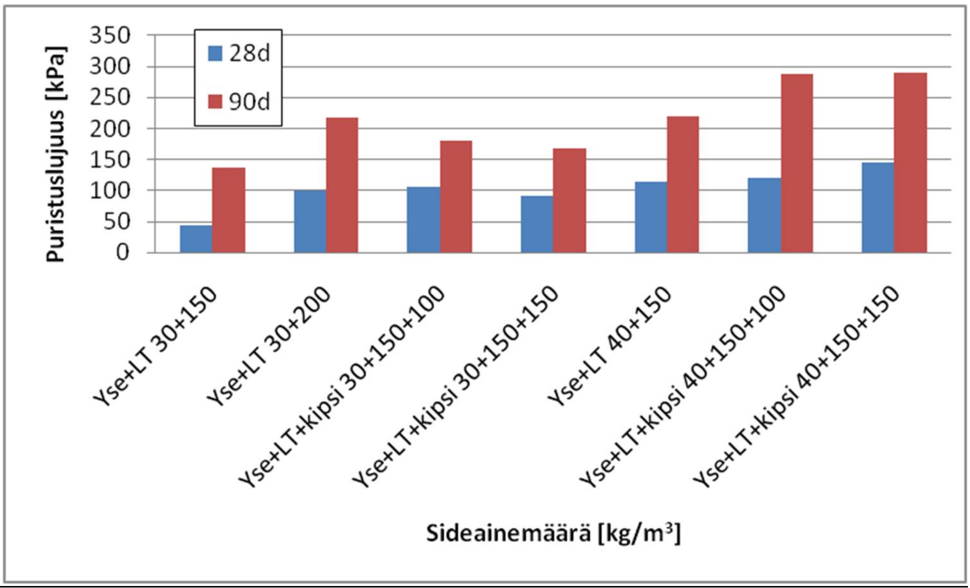

Figure 12. Functionality of cement-fly ash-gypsum mixture.

- Gypsum gives some extra strength on cement-fly ash –mixture, but increasing the amount of fly ash is more effective on compression strength than adding the amount of gypsum
- Time curing is significant.

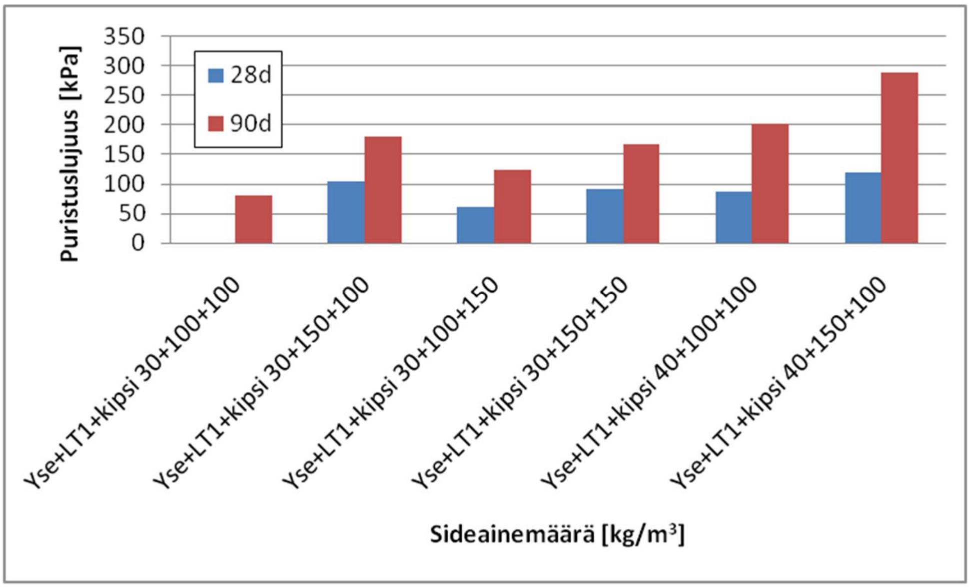

Figure 13. Functionality of cement-fly ash-gypsum mixture.

- Increasing the amount of fly ash with 50 kg/m^3 gives more strength than increasing the amount of gypsum with 50 kg/m^3

Cement-oil shale ash-gypsum mixtures

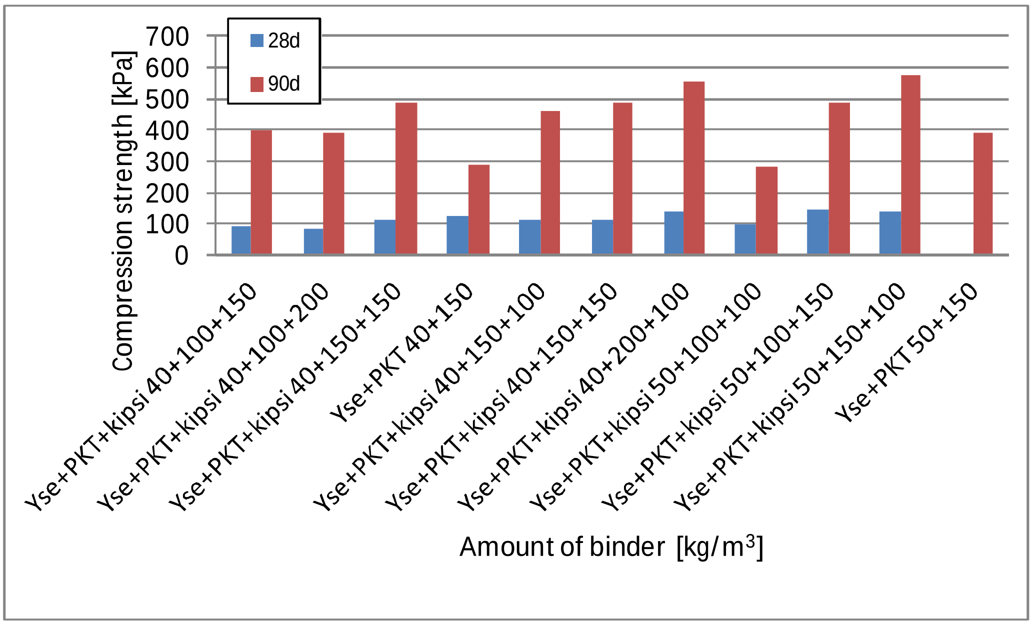

Figure 12. Compression strength of cement-oil shale ash-gypsum-mixtures

- Increasing the amount of oil shale ash is more effective than increasing the amount of gypsum in cement-oil shale ash-gypsum mixture
- Time curing is significant

Cement-blast furnace slag –oil shale ash-gypsum mixtures

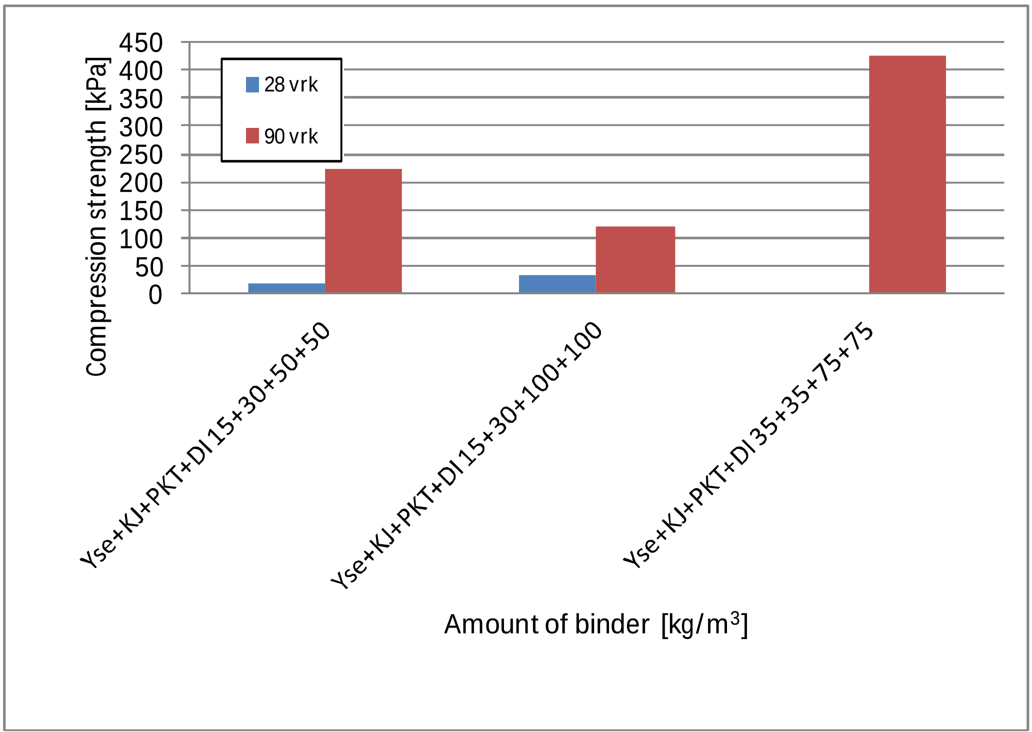

Figure 13. Compression strength of cement-blast furnace slag-oil shale ash-gypsum-mixtures

- Increasing of the amounts of oil shale ash and gypsum does not bring benefit

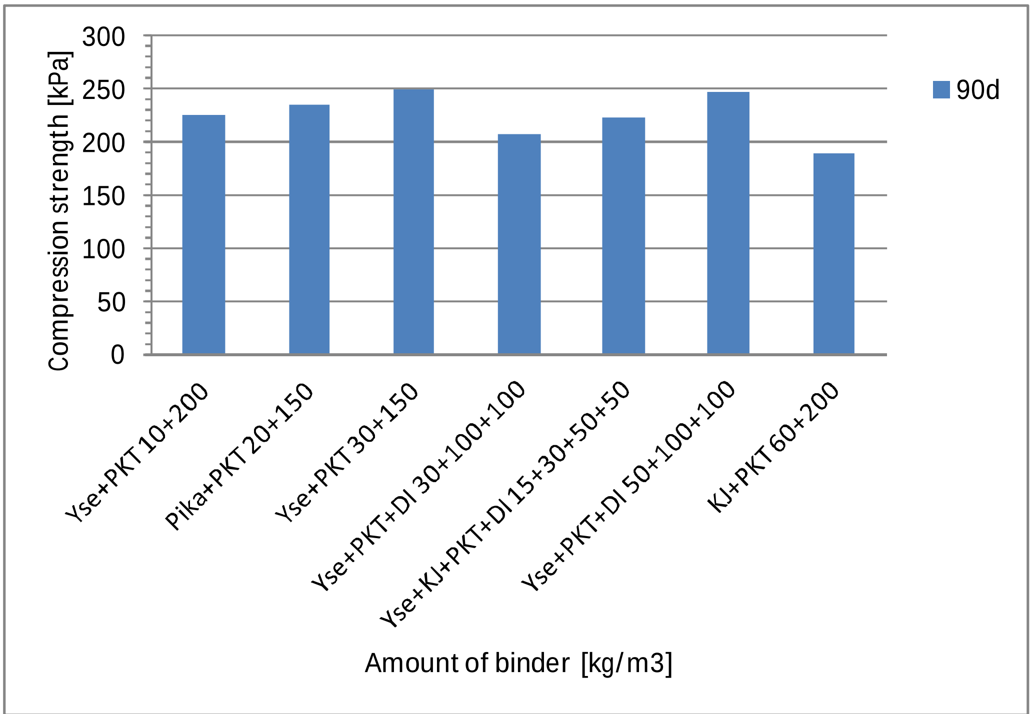

Figure 14. Binder mixtures to achieve 200-250 kPa strength in 90 days. The amount of commercial binder rises to the right.

- Target strength can be achieved with very low amounts of commercial binders

Effect of long-term strength development

Long-term strength development was studied with different binders: oil shale ash, YSe-gypsum-mixture, YSe-oil shale ash-mixture, YSe-oil shale ash-gypsum-mixture. Long-term strength development is shown in figure 15.

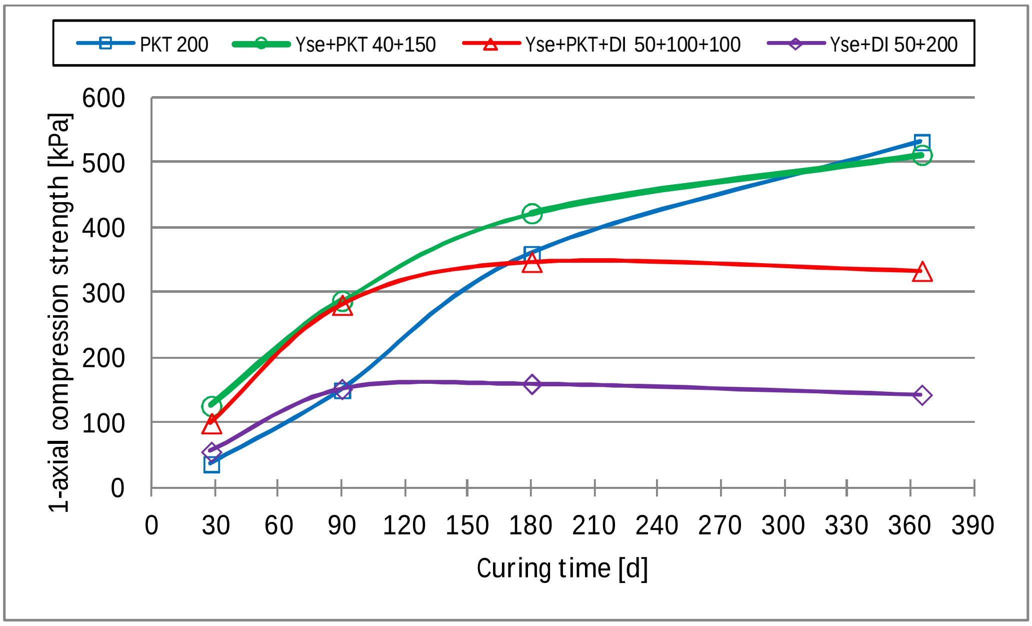

Figure 15. Effect of time curing.

- With oil shale ash and Portland cement-oil shale ash mixture the curing continues for one year
- Portland cement- oil shale ash-gypsum mixture reaches final strength in six months
- Portland cement- gypsum mixture reaches final strength in three months

7. RIVER KYMI

Sediments of River Kymi all the way from Kuusankoski to Gulf of Finland are contaminated with dioxins, furans and mercury. Total amount of PCDD/F-compounds is estimated to 6000 kg and 2800 kg of mercury. The amount of contaminated sediment is estimated to be 5 million m^3. Contamination is not homogenous, but instead in slower points of stream the soft sediments are contaminated. In those parts where river bottom is hard and coarse, sediments are not contaminated. Flow of the river transports contaminants slowly towards the Gulf of Finland.

7.1 Materials

Sampling area is located in Kuusankoski Power Plant downstream. The samples were taken by diver with tube and shovel. The geotechnical index properties are shown in table 10. The organic matter contents of sediment samples were high. Sediment samples contain for example organic fibres originated from forest industry carried on by the river.

Table 10. Geotechnical index properties of sediment samples

Sample	w [%]	ρ [kg/m³]	LoI [%]	pH	Soil type
P1	351	1140	21,3	6,2	Gyttja
P2	274	1180	15,6	6,2	silty gyttja
P3	275	1180	14,0	6,3	silty gyttja
Kokooma P1-P3	296	1170	16,9	6,3	silty gyttja

The used binders in stablisation tests were:

- Cement (YSe)
- Oil shale ash (PKT A)
- Slag furnace powder (KJ)
- Di-gypsum from Yara Suomi (DI)

7.2 Results

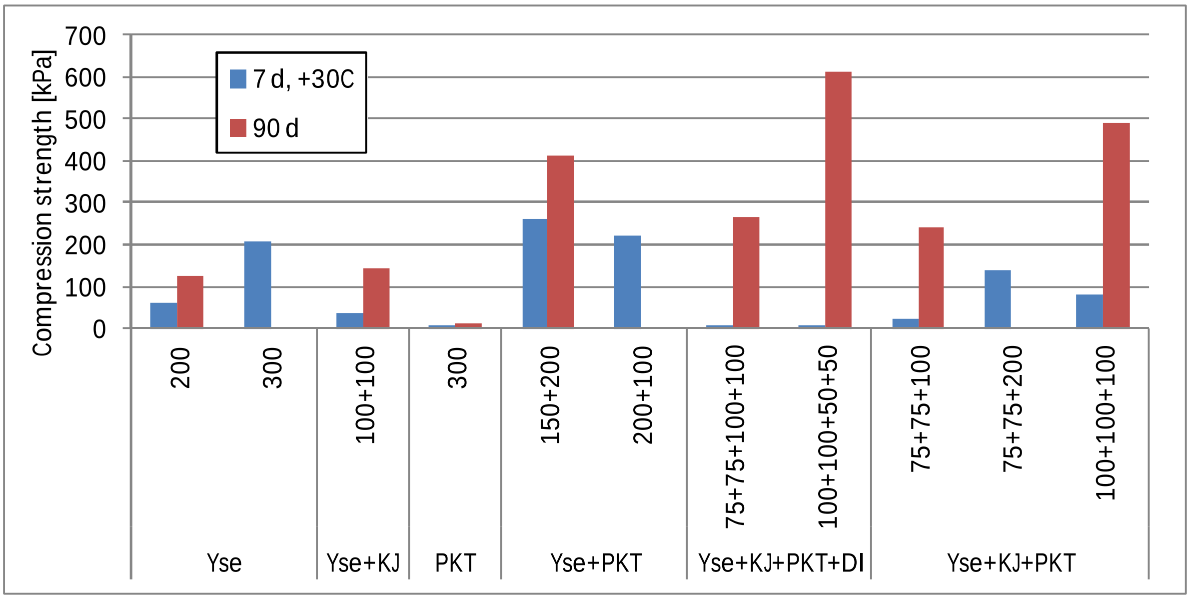

Figure 16. Compression strength results for sediment samples from River Kymi

Gypsum was combined with cement, blast furnace slag and oil shale ash. The highest compression strength result was obtained with mixture of Yse + KJ + PKT + DI 100+100+50+50 kg/m^3, when 90 days strength result after normal treatment was 614 kPa. With same recipe the 7 days thermal treatment result was < 10 kPa.

8. KLAIPEDA

Gypsum has been tested with sediments from Port of Klaipeda. The results from stabilisation tests are presented in report "Eesti Energia, Stabilisation test report for sediment samples from Port of Klaipeda, 17.8.2011, Ramboll Finland Oy".

8.1 Materials

The results of characterization tests are shown below in Table 11. Samples nr 1 and nr 2 as well as samples nr 5 and nr 6 were combined as aggregate samples.

Table 11. Characterization tests of sediment samples.

Sample code	Water content [%]	Bulk density [kg/m^3]	Ignition loss [%]	pH	Soil type	Notes
139 / nr 1	248	1210	10,8	8,0	gyttja (sand)	pH and grain size measured from aggre-gate sample nr1+nr2
139 / nr2	279	1190	12,3			
65 / T3	131	1360	4,4	7,7	silty sand (humus)	
65 a / nr 4	70	1580	3,9	7,9	sand (humus)	
58 / nr 5	175	1290	7,7	7,8	silty gyttja	pH and grain size measured from aggre-gate sample nr5+nr6
58 / nr 6	142	1330	5,7			

Three oil shale ash samples were used as binder material in stabilization tests as well as cement and gypsum. Binders used in the stabilization tests are:

- Portland cement (Yleis)
- gypsum (KI)
- oil shale cyclone fly ash (PKT c)
- oil shale bottom ash (PKT ba)

- oil shale electric filter fly ash (PKT ef)

8.2 Results

Stabilization tests were done for 4 different sediment samples. Two of them were "main samples" to which 15 different binder recipes were tested. Samples were tested after 90 days of normal treatment (+8 ^{0}C) and after 4-6 and 28 days of thermal treatment (+30 ^{0}C).

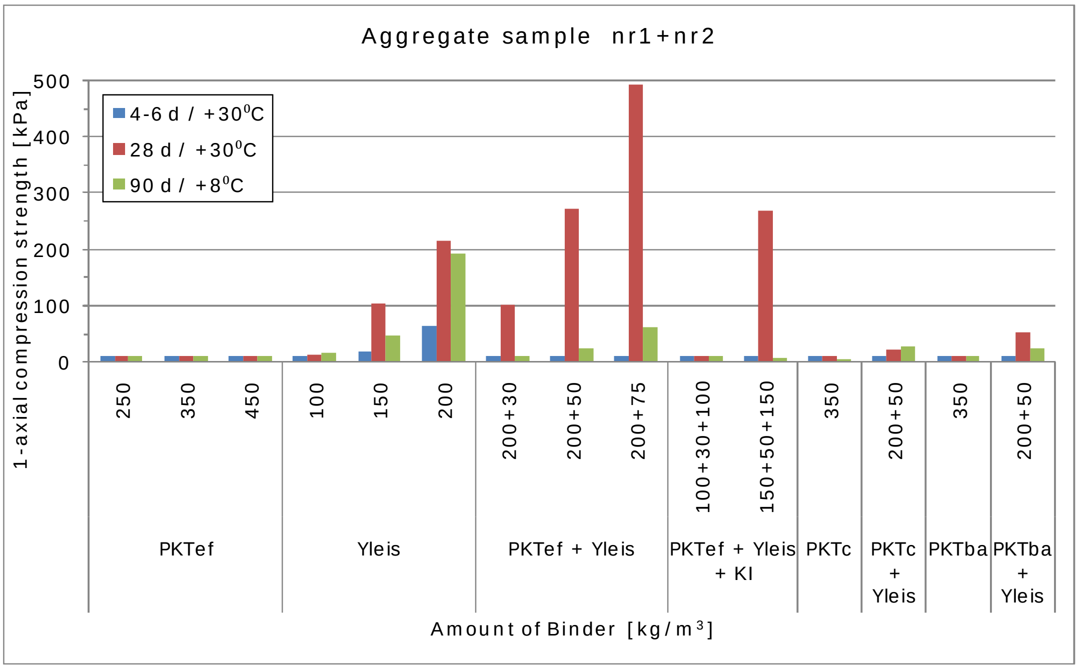

Figure 17. Results of stabilisation tests for aggregate sample nr1+nr2

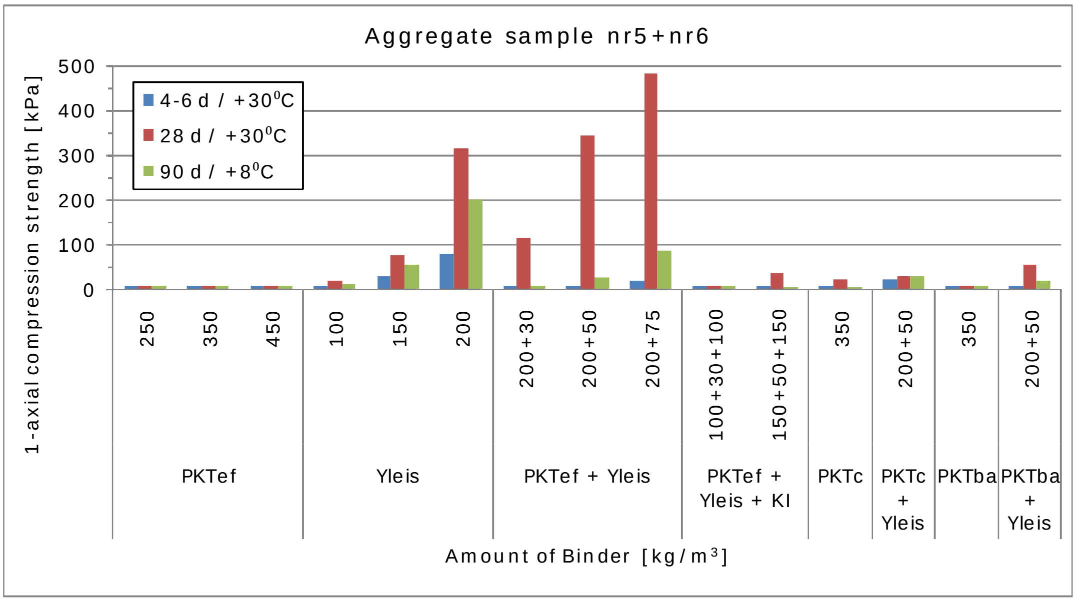

Figure 18. Results of stabilisation tests for aggregate sample nr5+nr6

The results show that:

- The amount of cement needed for stabilization is high; approximately 200 kg/m^3, if 200 kPa is the target level for 1-axial compression strength.
- 28 days of thermal treatment in +30^{0}C shows the long-term curing potential of the binder mixtures. In most recipes the strength in 90 days of normal treatment is much lower than the 28 days thermal treatment results. It means that the 28 days thermal treatment results predict the curing potential of recipes for much longer period of time than 3 months.
- 4-6 days of thermal treatment was too short curing time for most of the binder recipes
- According to 28 days thermal treatment results gypsum (Kl) is working as a binder material with cement and oil shale ash
- The higher water content (w) and organic matter content (LoI) of sediment sample, the lower is the strength of stabilized test piece.

- The contaminants of the sediment samples can have an effect on curing of sediment-binder mixtures. The samples tested in this study seemed to be contaminated with mineral oil. The content of contaminants was not investigated in this study, but the smell and the colour of the sediment samples suggested that samples contained oil.

9. GDYNIA

Gypsum has been tested with sediment sample from Port of Gdynia. The results from stabilisation tests are presented in report "Port of Gdynia, Stabilisation test report, 3/2011, Ramboll Finland Oy".

9.1 Materials

The results of characterization tests of sediment samples are shown in Table 12. Aggregate sample was used as base material in stabilisation studies.

Table 12. Characterization tests of sediment samples.

Sediment sample	w [%]	ρ [kg/m^3]	LoI [%]	pH
GD 1.b6	167	1300	7,6	7,5
GD 2.b6	201	1250	9,2	7,4
GD 3.b6	171	1290	8,9	7,6
GD 4.b6	125	1380	6,6	7,7
GD 5.b6	100	1450	7,0	7,8
GD 6.b6	164	1300	9,1	7,6
GD 7.b6	167	1290	9,0	7,5
GD 9.b6	153	1310	7,7	7,5
Aggregate sample*	169	1290	9,0	7,5

* Aggregate sample is a combination of samples 1, 2, 3, 6, 7 and 9.

Following binders were used in stabilisation studies:
- Yse = Ordinary Portland Cement (CEM II/A-M(S-LL) 42,5 N)
- PKT = Oil shale fly ash from Eesti Energia (Estonia)
- KJ = Blast furnice slag (Finland)
- DI =Diphosphate Gypsum from Yara (Finland)

9.2 Results

The results for stabilisation studies are shown in figure 20.

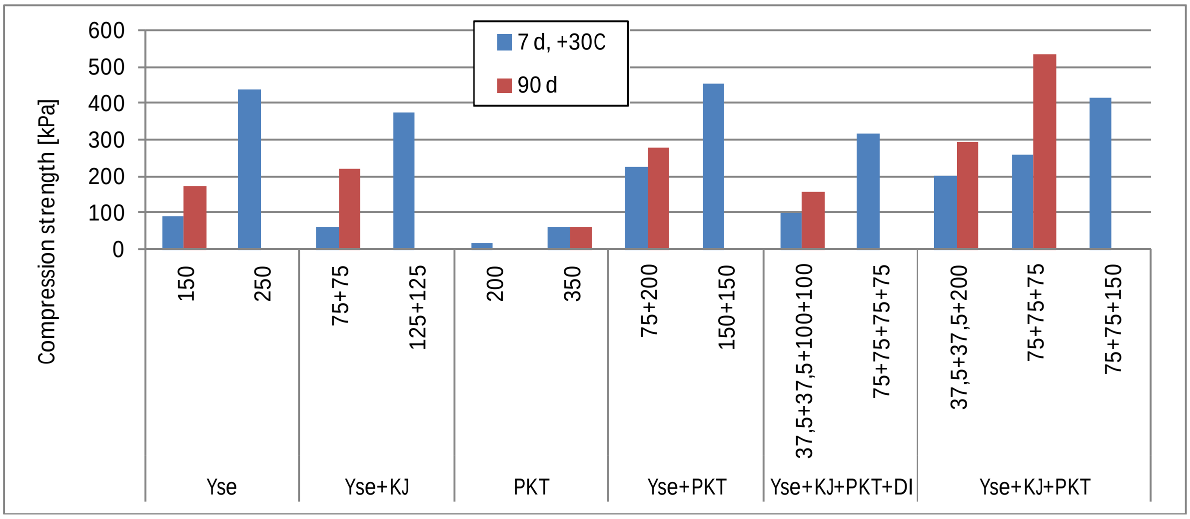

Figure 20. Compression strength results for sediment from Port of Gdynia

Gypsum was combined with cement, blast furnace slag and oil shale ash. 7 days thermal treatment result was good with mixture where 75 kg/m^3 of every binder were mixed. The result was 315 kPa (average from 292 kPa and 338 kPa), which indicates that long time curing is significant. With this binder mixture the test specimen was not tested for 90 days compression strength. Also with mixture of those four binders (Yse + KJ + PKT + DI) with amounts of 37,5+37,5+100+100 kg/m^3 the 90 days compression strength was 156 kPa when the target strength was 100-200 kPa.

10. SUMMARY OF TECHNICAL PART

West Harbour in Helsinki (Jätkäsaari)

- The sediment material is easily strengthened with low binder amount
- High compression strength values can be obtained by using gypsum together with oil shale ash and cement.
- Yara gypsum is a potential binder option for sediments of Jätkäsaari. With use of gypsum it is possible to obtain clear advantages in compression strength results.
- The most ideal binder mixture is lime cement-gypsum-mixture. The amount of gypsum is 1/3 of the amount of lime cement. If the portion of gypsum is higher, the compression strength results get lower.
- In large projects as in case Jätkäsaari, the use of gypsum brings remarkable advantages when it comes to binder costs and strengthening results.
- When potential of gypsum is estimated, the water content of gypsum has to be observed. If process stabilization method is used, the moisture of gypsum is not a problem, but in mass stabilization method the binder should be totally dry if special arrangements are not possible for the feed of moist gypsum.

Fairway of Kokkola

- The thermal treatment results were good (28 d), but normal 28 d results were quite low in most cases.
- Gypsum combined to oil shale ash doesn’t work for sediments of Fairway of Kokkola.
- When gypsum is combined to cement, oil shale ash and fly ash, good compression strength values are obtained. The amount of binders is quite high although.
- The results for combination of cement, oil shale ash and gypsum show that the amount of cement have to be sufficient (at least 50 kg/m^3) in order to achieve reasonable strength.

Port of Kokkola, Deep Port

- The thermal treatment samples show that the gypsum especially mixed with ashes has potential for high compressive strengths after long strength development period. A good thermal treatment result usually indicates good long time curing results.
- Good compressive strengths can be achieved with small cement amount (30 kg/m^3) when oil shale ash, gypsum and fly ash are used in addition. The stabilization can be done with for example with process stabilization equipment.

River Kymi

- The water content and organic matter content of sediment is high and as a result higher binder amounts are needed than for other sediments tested
- When gypsum is combined with cement, slag furnace powder and oil shale ash, good compression strength values are obtained but the amount of commercial binders has to be quite high (approx. 75-100 kg/m^3) in the mixture.
- Gypsum brings extra benefit to strength when combined with cement and oil shale ash.
- Time curing is significant.

Port of Klaipeda

- Gypsum was used together with oil shale ash and cement. The best strength result (28 d thermal treatment: 269 kPa) was achieved with mixture these binders with amounts of oil shale ash 150 kg/m^3 + cement 50 kg/m^3 + gypsum 150 kg/m^3. Although 28 days thermal treatment result was good, result after 90 days normal treatment was only 7 kPa.
- Gypsum didn’t work with Klaipeda sediments.
- The amount of cement was too low in tested cement-gypsum-oil shale ash mixtures and as a result the compression strength values were low. Probably the compression strength values would have been good when the amount of cement would have been about 100 kg/m^3 in the cement-gypsum-oil shale ash mixtures.
- The contaminants of the sediment samples can have an effect on curing of sediment-binder mixtures. The samples tested in this study seemed to be contaminated with mineral oil. The content of contaminants was not investigated in this study, but the smell and the colour of the sediment samples suggested that samples contained oil.
- The effect of water content of sediment on strength was obvious

Gdynia

- Cement-slag powder-gypsum binder mixtures gave the best compressive strength results.
- According to stabilization tests the following binder mixtures are most potential for stabilization: cement 75 kg/m^3 + blast furnace slag 75 kg/m^3 + gypsum 75 kg/m^3 and cement 75 kg/m^3 + fly ash Gdynia 75 kg/m^3 blast furnace slag 75 kg/m^3 + gypsum 75 kg/m^3
- The water permeability was 2,6 x 10^{-9} with cement 75 kg/m^3 + fly ash Gdynia 75 kg/m^3 blast furnace slag 75 kg/m^3 + gypsum 75 kg/m^3 stabilizes specimen

11. CONCLUSIONS

Gypsum is a potential binder option when it is used together with other industrial by-products and cement. As in case with other binders, also gypsum needs specific tests and recipes for each case before its applicability and potential of use is surely known. Depending on the case and properties of the sediment to be stabilized, it is possible to achieve clear advantages on strengthening and costs when gypsum is used.

However, if water content or organic matter content of the sediment is high, the amount of binders needed is quite high. In any case by using gypsum the demand of cement and other commercial binders are reduced considerably. That saves binder costs.

In most cases gypsum works best together with oil shale ash and cement. The amount of gypsum is quite accurate, and usually addition of gypsum doesn’t bring any benefit to compression strength. Exception for this is sediment from River Kymi were addition of gypsum was beneficial to strength.

The effect of gypsum on strength is obvious, but for the best results, gypsum has to be tested case by case.