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BEHAVIOUR OF COBALT IN WATER TREATMENT

Degree Programme in Environmental Engineering
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KOBOLTIN KÄYTTÄYTYMINEN VESIENKÄSITTELYSSÄ

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TIIVISTELMÄ

Tämän opinnäytetyön tarkoituksena oli tutkia koboltin ja nikkelin käyttäytymistä vesienkäsittelyprosessissa. Tavoitteena oli löytää keinoja, joilla Norilsk Nickel Harjavalta Oy vesienkäsittelyprosessiin ohjattavien nykyisten prosessivesien lisäksi prosessiin voitaisiin ohjata uusia kobolttipitoisia jakeita. Samalla voitaisiin parantaa nykyprosessin toimintaa.

Opinnäytetyössä on tutkittu koboltin ja nikkelin käyttäytymistä karbonaatti – ja hydroksidisaostuskokeissa, sekä niiden käyttäytymistä laskeutumiskokeissa. Saostus käsitti kolme eri koetta: karbonaattisaostus, hydroksidisaostus, sekä yhdistetty karbonaatti – ja hydroksidisaostus. Laskeutumiskokeet sisälsivät testejä mahdollisilla uusilla jakeilla, vesienkäsittelyprosessiin tulevilla prosessivesillä ja edellä mainittujen jakeiden yhteisliuoksilla. Apuaineina käytettiin ferrisulfaattia, puhallushiekkaa ja piimaata. Osana opinnäytetyötä oli myös täyden mittakaavan koe, jossa puhallushiekkaa käytettiin tehostamaan vesienkäsittelyprosessia.

Opinnäytetyössä saadut tulokset olivat suuntaa antavia. Saostumiskokeet osoittivat, että kaiken koboltin pitäisi saostua vallitsevissa olosuhteissa vesienkäsittelyprosessissa. Kokeiden perusteella voidaan todeta, että tulevaisuudessa jatkokokeita voidaan suorittaa ainakin piimaalla, joka antoi parhaat tulokset.

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ABSTRACT

The purpose of this thesis was to investigate the behaviour of cobalt and nickel in water treatment process. The main aim was to discover means if other cobalt containing fractions, in addition to the standard incoming process waters, could be directed to the water treatment process. This could also benefit the function of the current process.

Behaviour of cobalt and nickel was studied in precipitation and settling experiments. Precipitation experiments included carbonate, hydroxide, and combined carbonate – hydroxide precipitation. The settling experiments included three parts: the settling of possible new fractions, the settling of standard input waters and the settling of joint solutions containing both possible new fractions and standard input waters. The settling agents were ferric sulphate, silica sand, and diatomite. Part of this thesis was a full process scale experiment, where silica sand was utilized in the part of water treatment process.

The results received could be considered to be more or less indicative. The precipitation experiments indicated that all cobalt should precipitate during the water treatment process. According to the results it is evident that in the future it is recommended to carry out experiments at least with diatomite, which gave the best results.

CONTENTS

APPENDIX 1: RESULTS OF THE PRECIPITATION EXPERIMENTS

APPENDIX 2: RESULTS FROM THE SETTLING EXPERIMENTS NIPK1, NIPK3 AND CUIX

APPENDIX 3: RESULTS FROM THE SETTLING EXPERIMENTS SI, NIPK1, NIPK3 AND CUIX

APPENDIX 4: RESULTS FROM THE SETTLING EXPERIMENTS SI, NIPK1, NIPK3 AND CUIX 30MIN REACTION TIME WITH FERRIC SULPHATE

LIST OF SYMBOLS

RE 3701	Water treatment precipitation reactor 1
RE 3702	Water treatment precipitation reactor 2
RE 3703	Water treatment precipitation reactor 3
SAK 3701	Water treatment thickener
NiPK1	Extraction scrubbing water 1
NiPK3	Extraction scrubbing water 3
CuIX	Ion exchange resin flushing water
ICP3	Water analyzer
LS 283	Process water pipeline 1
PS 323	Process water pipeline 2
VS 3851	Chemical plant process water container
PVA	Process water pool
SVA	Rainwater pool
JTS 3651	Waste water expansion tank

1 INTRODUCTION

The purpose of this thesis was to examine the behaviour of cobalt and nickel in water treatment process in order to improve the effectiveness of cobalt and nickel removal in Norilsk Nickel Harjavalta Oy water treatment plant. The aim was to examine if the some alternative settling agents could improve the sedimentation in the water treatment process. Moreover, the aim was to examine the removal of cobalt and nickel by carbonate –and hydroxide precipitation, and the effectiveness of cobalt and nickel removal by using settling agents in the settling experiments. One part of the thesis was to investigate if some settling agents could be utilized in a production scale as a part of water treatment process.

This thesis was done in order to investigate if new possible fractions could be added to the water treatment process and thus improve the effectiveness of the whole process. In this thesis the goal was to investigate if concentrations of cobalt and nickel could be decreased by settling the precipitated cobalt and nickel particles more effectively with the help of alternative settling agents. Ferric sulphate and a flocculent are already utilized to improve the sedimentation in Norilsk Nickel Harjavalta Oy water treatment plant but this thesis investigated whether some other settling agents could be utilized as well.

This thesis includes a theoretical part that explains the theory behind the water treatment processes and some theoretical information about cobalt, nickel and alternative settling agents, and an experimental part that shows the experiment done in this thesis and their results. The laboratory experiments were conducted in Norilsk Nickel Harjavalta Oy research laboratory.

2 NORILSK NICKEL HARJAVALTA OY

Norilsk Nickel Harjavalta Oy is a nickel chemical and nickel metal manufacturer company in Harjavalta, Satakunta. It belongs to the world's largest nickel manufacturer, Russian mining and metallurgical company MMC Norilsk Nickel Group. Main products of Norilsk Nickel Harjavalta are different kind of high-technology nickel products; such as nickel briquettes, nickel cathodes and nickel chemicals. The number of employees in the factory is about 270.

The production process in Norilsk Nickel Harjavalta Oy includes four different sections: leaching, extraction and reduction, electrolysis, and chemical plant. In leaching cobalt is leached with nickel as a sulphate solution and in extraction they are separated to cobalt sulphate and nickel sulphate. After this the final products will be produced from the solutions in reduction, electrolysis and chemical plant. The raw materials come from Southern countries; such as South Africa, Brasilia and Australia. About 29 percent of nickel raw material comes from Talvivaara mining company in Finland. (Website of Norilsk Nickel Harjavalta Oy 2014)

3 COBALT

3.1 Cobalt and Its Usages

Cobalt is a silvery grey element that has atomic number 27 and it occurs naturally. Cobalt can be found in nature from surface water, soil, groundwater, sediments and leachates from hazardous waste sites. Cobalt has only one stable isotope, Co-59, and 26 known radioactive isotopes. Cobalt can occur in the 0, +2, and +3 valence states. The relative molecular mass of cobalt is 58.93 and in the room temperature cobalt is solid. In the mined ore there is only about 0.1% element cobalt and the normal associations for cobalt are copper and nickel. In the world cobalt production about 44% comes from nickel ores. Ways to extract cobalt from the metals in the ore are flotation, gravity, pyrometallurgical methods, and hydrometallurgical methods. In 2003 the total cobalt mine production was 46 900 tons and the approximate amount of refined cobalt was 43 000 tons. (Kim, et al. …2006, 4- 8)

Cobalt is used to produce alloys, magnets, cutting and grinding tools, and in artificial hip and knee joints. Some cobalt compounds can also be used to color glass, ceramics and paints, and also as drier porcelain enamel and paints. Radioactive Co-60 can be used in commercial and medical purposes, such as for sterilizing medical equipment, treating cancer with radiation therapy, manufacturing plastics, and irradiating food. (Website of Lenntech 2014)

Norilsk Nickel Harjavalta Oy produces at the moment cobalt sulphate as their cobalt product. Cobalt sulphate contains about 21 percent cobalt. (Website of Norilsk Nickel Harjavalta Oy 2014)

3.2 Behavior of Cobalt in Water Treatment Processes

Released into the water bodies cobalt may sorb to particles and then settle to the sediments or sorb straight to the sediments. The amount of cobalt precipitating from the water to sediments depends on pH, redox conditions, dissolved organic matter concentration and ionic strength. Average level of cobalt in drinking water is 2 µg/l and the highest reported values have been up to 107 µg/l. (Website of EPA United States Environmental Protection Agency 2013)

4 NICKEL

4.1 Nickel and Its Usages

Nickel is a silvery-white chemical that has atomic number 28. In the earth’s crust nickel is the 24th most often occurring element. Nickel can be found from different ores such as oxides, silicates, and sulphides. Nickel can be found in nature from continental windblown dust, volcanic dust and gases. Nickel can occur in many valence states, such as 0,+2,+3 states. The relative molecular mass of nickel is 58,693 and in the room temperature nickel is solid.

Nickel is used to produce steel, alloys, nickel sulphate and nickel chloride in electroplating, coinage as a catalyst, ceramics, storage batteries as nickel hydroxide, coloring class, electronic components-, and food processing equipment. Nickel is also used to produce stainless steel with the usual portion of 8% nickel. (Sharma 2012, 16-19)

4.2 Norilsk Nickel Harjavalta Oy Nickel Products

Norilsk Nickel Harjavalta Oy manufactures large scale of high.-technology nickel products. Product groups include nickel cathodes, nickel briquettes, nickel suphate, nickel hydroxide, nickel hydroxide carbonate-, and ammonium sulphate.

Nickel cathodes comprise about 29 percent of the plant’s production. Nickel cathodes contain 99.9 percent of nickel and they are used to manufacture coatings and alloy metals, especially stainless steel. Nickel briquettes comprise about 58 percent of the plant’s production. Nickel briquettes contain 99.8 percent of nickel and they are used for example in stainless steel production. Nickel chemicals: nickel sulphate, nickel hydroxide and nickel hydroxide carbonate comprise together 13 percent of the plant’s production. Nickel sulphate contains about 22 percent nickel and it is used in electroplating and tinting of anodized aluminium. Nickel hydroxide contains about 62 percent nickel and it is used in battery industry. Nickel hydroxide carbonate contains about 40-50 percent nickel and it is used in corrosion prevention and in the electronics and chemical industry. Ammonium sulphate is a by-product of nickel production and it is used as a fertilizer. (Website of Norilsk Nickel 2014)

4.3 Behavior of Nickel in Water Treatment Processes

Elemental nickel is insoluble in water although many nickel salts are readily soluble in water and thus water systems can be contaminated by nickel. Nickel Ni (II) is both toxic and carcinogenic so WHO (World Health Organization) has set limits to

Ni (II) in drinking water to be 0,02mg/l. Methods to remove heavy metals from wastewater include oxidation, reduction, precipitation, membrane filtration, ion exchange, and adsorption. (Sharma 2012, 16-19)

5 WATER TREATMENT PROCESS IN NORILSK NICKEL HARJAVALTA OY

5.1 Water Treatment Process Description

Water treatment process in Norilsk Nickel Harjavalta Oy includes the purification of process waters and rainwaters collected from the factory area. The purification process includes precipitation of nickel and other heavy metals with sodium hydroxide and sodium carbonate, followed by thickening and filtration of the precipitate. Water treatment process includes sand filtration and process water pool as a final settling step before releasing the waters into the river. The solution discharged to the river is sodium sulphate.

Water treatment process starts with precipitation. Sodium hydroxide is added to the precipitation reactors in order to increase pH to target level that is slightly above 10. At this stage also ferric sulphate is added. From the third reactor the precipitated input waters go to the thickener, SAK 3701, where the sediments are separated. Flocculent is added in order to improve the sedimentation. After the sedimentation process overflow water flows through the sand filtration and from there to the process water pool or to the clean water pool. If the pH of water and the concentration of nickel and other chemicals are as regulated, water from the clean water pool is discharged to the river. The process is monitored constantly and samples of the waters are taken daily. (Sallinen, Ruusunen, Alisaari 2014, 33-36)

5.2 Chemical Precipitation Process

5.2.1 Chemical Precipitation

Certain soluble inorganic materials can be removed from the solution by adding reagents that convert those soluble materials into insoluble precipitates and filtrate. Chemical precipitation is used to remove heavy metals from the industrial waste -and process water. The effectiveness of the removal depends on the solubility of the materials and factors as pH and temperature. (Tebbutt 1998, 212)

The most widely used chemical precipitation techniques are hydroxide, carbonate, and sulfide treatments. From these techniques the hydroxide precipitation is most commonly used because of the low cost of the precipitant, relatively simple process and the automatic pH control. Hydroxide precipitation removes almost completely iron manganese, copper, zinc, nickel and cobalt. Many metals are amphoteric and thus in the appropriate pH conditions (8.0 to 11.0) the solubilities of the metal hydroxides are low and precipitation occurs. Removal of metals by using hydroxide precipitation may not be effective, if there are waste containing mixed metals because the metals have different minimum solubilities in the different pH values. In comparison with hydroxide precipitation technique carbonate precipitation occurs at lower pH conditions. Solubilities in carbonate precipitation are relatively low at high pH values. Solubilities of nickel and cobalt as carbonates and hydroxides are presented in Figures 1 and 2. In the Figure 1 carbonate precipitation have been done with 1bar carbon dioxide partial pressure. (Peters, Ku, Bhattacharyya, 166-168)

Hydroxide precipitation follows usually the reaction:

$$M^{+n} + nOH^{-} \leftrightarrow M(OH)_n \qquad (1)$$

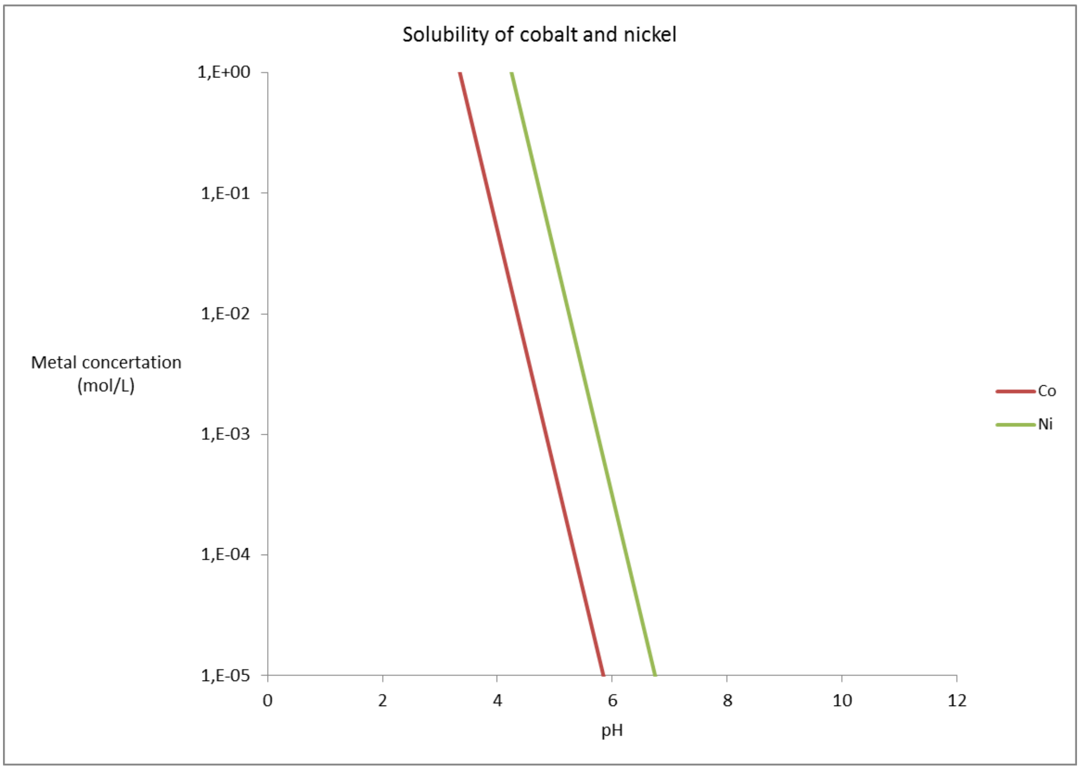


Figure 1. Solubility of carbonates

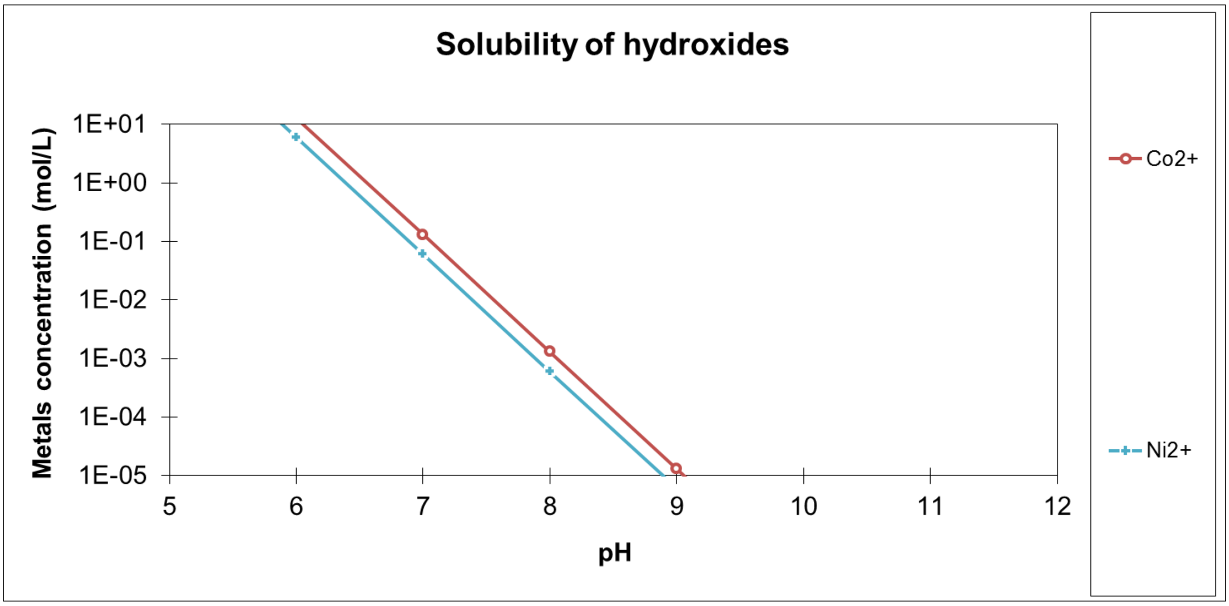


Figure 2. Solubility of hydroxides (Anttila, et al. …1986)

From the Figures 1 and 2 can be seen that the solubilities of nickel and cobalt decrease when pH values are increased. Metal concentrations are relatively low when the pH values are high enough. In carbonate precipitation the precipitation of cobalt and nickel started at lower pH values than in hydroxide precipitation but hydroxide precipitation was more effective compared to carbonate.

Sodium Carbonate, Na_2CO_3

Sodium carbonate is white and odorless chemical in the form of powder, grain or pellets. Sodium carbonate is used in Norilsk Nickel Harjavalta Oy in, for example, the production of nickel hydroxide carbonate and nickel hydroxide and it can be used also in the water treatment process. In aqueous solution sodium carbonate is strongly alkaline and it can cause irritation if contacted with the skin or eyes. (Sallinen, Ruusunen, Alisaari 2014, 41)

5.2.1.1 Sodium Hydroxide, NaOH

Sodium hydroxide is colorless and odorless chemical. Sodium hydroxide is used in Norilsk Nickel Harjavalta Oy in the production of demineralized water for pH adjustment, in the process water treatment and in the production of nickel hydroxide. In aqueous solution sodium hydroxide is strongly alkaline and highly dangerous if in contact with eyes. Sodium hydroxide is corrosive for aluminum, magnesium, zinc, tin, lead, and for their alloys releasing hydrogen gas. Sodium hydroxide reacts strongly with acids. In water bodies sodium hydroxide is mildly dangerous because it causes rapid increase in pH. (Sallinen, Ruusunen, Alisaari 2014, 41-42)

5.2.2 Chemical Precipitation as a Part of Norilsk Nickel Harjavalta Oy Water Treatment Process

Precipitation of process waters and its metals occurs in three reactors, RE 3701/3702/3703, connected in series. Sodium hydroxide and possibly sodium carbonate are added in order to increase pH to sufficient level. Sodium hydroxide is added to the first reactor, RE 3701, to meet the pH index value. Solution flows to the reactor RE 3702 as overflow. Sodium hydroxide is added to the reactor through the flow rate controller until the pH is slightly over 10. Solution flows to the reactor RE 3703 as overflow from where it is directed to the thickener, SAK 3701, by using pumps. (Sallinen, Ruusunen, Alisaari 2014, 33)

5.3 Coagulation and Flocculation Process

5.3.1 Coagulation

Coagulation process includes adding coagulants into the solutions in order to build up particle size and thus enable bigger particles to sediment to the bottom. Coagulation is based on the different charges particles have. Colloids form with the help of coagulants microflocks. In coagulation chemical coagulants are added into the raw/process water and mixed rapidly.

In coagulation process there are two different kind of chemicals used: coagulants and coagulant aids. Usually particles that need to be removed are negatively charged and thus the coagulants used in water treatment are mostly positively charged ions in order to neutralize the negative charges and enhance coagulation. Coagulants used in coagulation are typically trivalent cation compounds such as: aluminum sulfate ($Al_2(SO_4)_3$), aluminum chlorohydrate ($AlCl_3x\ H_2O$) and iron salts like ferric chloride ($FeCl_3$), ferric sulfate ($Fe_2(SO_4)_3$). Coagulant aids are used to improve the coagulation process. Coagulant aids can improve to build stronger and more settleable flocks, reduce the amount of coagulant needed or reduce the amount of sludge produced. (AWWA Staff 2010, 47-54)

5.3.2 Flocculation

Flocculation process includes adding flocculants into the solutions in order to build up particle size and thus enable bigger particles to sediment to the bottom. This process enables weakly settable solids to convert into larger and heavier settleable solids. After settling, solids can be removed by the sedimentation and filtration processes. In flocculation the mixing of chemicals and water is slow in order to assist in building up particle size. Flocculation process enables the microflocks to generate larger and heavier particles, macroflocks. (AWWA Staff 2010, 63-64)

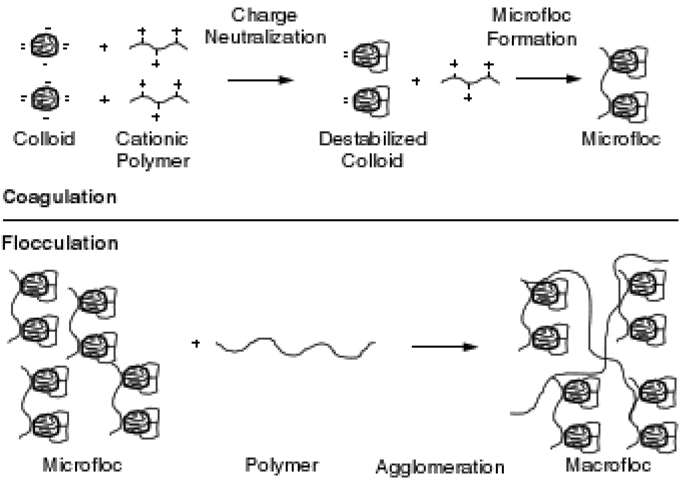


Figure 3. Coagulation and Flocculation (AWWA Staff 2010, 50)

5.3.2.1 Ferric Sulphate, $Fe_2(SO_4)_3$

Ferric sulphate is used in both industrial and municipal wastewater treatments as coagulant and flocculent. In aqueous solution ferric sulphate is red-brown liquid. In water treatment process ferric sulphate is added in order to improve clarification by forming rapidly settling flocks. (Website of Generalchemical 2014)

Ferric sulphate is acidic and moderately corrosive. In Norilsk Nickel Harjavalta Oy ferric sulphate is used in demineralized water production to decrease the amount of solids in raw water and in the water treatment process as a coagulant. (Sallinen, Ruusunen, Alisaari 2014, 41)

5.3.2.2 Flopam FO 4125 SH

Flopam FO 4125 SH is a flocculent that is used for drainage of sludge, as a retention material, in water removal, and as a dewatering fastener agent. In Norilsk Nickel Harjavalta Oy this flocculent is used in water treatment in order to improve the sedimentation process. Flopam FO 4125 SH does not cause harm if in contact with skin or if breathed or swallowed but can be irritated if in contact with eyes. (Sallinen, Ruusunen, Alisaari 2014, 34 and SFN Finland Oy Käyttöturvallisuustiedote, 2011)

5.3.3 Coagulation and Flocculation in Water Treatment Processes

The characteristics of water affecting to the selection of coagulants and coagulation aids are type and concentration of contaminants, water temperature, pH, alkalinity, turbidity, color and total organic carbon.

Water temperature should be adjusted carefully because lower-temperature water causes usually poorer coagulation and flocculation, requires extended time period or more chemicals added. Low alkalinity may limit the coagulation and flocculation process because alum and ferric sulfate interact with those chemicals that cause alkalinity in the raw/process water. This reduces the alkalinity and the formation of aluminum and iron hydroxide complexes that start the coagulation process. If the turbidity of the water is low, the formation of flocks is more difficult because the amount of the collisions between particles is low and the possibility of particles to accumulate is slighter. In this case it might be necessary to add some weighting agent to water. (AWWA Staff 2010, 47-64)

5.4 Sedimentation Process

5.4.1 Sedimentation

As a part of water treatment sedimentation process removes sand, grit, chemical precipitates, pollutants, and other solids by gravity. The velocity and turbulence of the flowing water are reduced and thus the solids having greater mass settle to the bottom. Sedimentation process occurs in sedimentation/settling basin or tank. In water treatment processes the conventional place, where the sedimentation takes place, is between flocculation and filtration in order to reduce the load on filtration. For effective sedimentation process must be ensured the decent amount of coagulant and flocculent. The time that takes particle to pass through the basin, detention time, is dependent on the water treatment process but is usually designed to be near four hours. (AWWA Staff 2010, 81-84)

5.4.2 Sedimentation as a part of Norilsk Nickel Harjavalta Oy water treatment process

From the third precipitation reactor, RE 3703, precipitated solution is directed to the thickener, SAK 3701, where the most part of the sediments are separated. Flocculent is added to the thickener in order to improve the sedimentation. The targeted amount of the flocculent is about 1,5g/m^3. Sediments that contain nickel particles settle to the bottom of the thickener. Sediments are filtrated and washed in band filter. The overflow from the thickener is directed to sand filters. (Sallinen, Ruusunen, Alisaari 2014, 34)

5.5 Alternative Settling Agents

To form some additional particles and to improve formation of flocks, some settling agents could be added to water. If the water is high in color, low in turbidity and low in mineral content, settling agents are used to produce larger and more quickly settling flocks. (AWWA Staff 2010, 54-55)

5.5.1 Silica Sand

Sand usually refers to granular material consisting of natural minerals. Silica, also called quartz, (silicon dioxide, SiO_2) is usually the most dominant constituent of sand. Other natural minerals found in silica sand are feldspars, carbonates, iron dioxides, micas, clay minerals, and coal. Silica sands are commonly used in industry for different functions depending on their composition and physical properties, such as grain size, shape, sorting, specific gravity, and weight. Industrial uses for silica sands can be categorized as following: an abrasive in blasting and scouring sand, building products such as tiles and sand-lime bricks, glassmaking, hydraulic fracturing in oil well reservoirs, refractory agent in foundry and molding sands. (McLaws 1971, 2-3)

Determining the sand grain size, shape, and distribution must be noticed that the amount of sand surface is contributed by the grain shape and that the permeability of sand is controlled by grain size distribution. The shape of the grains varies so that the angular sand grains have the greatest surface-area-to-volume ratio and on the other hand rounded grains have a low surface-area-to-volume ratio. When the size distribution of the sand grains expands, more small sand grains fill in the spaces between larger grains. In foundry sands having the grain size 220-250µm are most commonly used. Fine silica sand, below 5 µm, can cause respiratory troubles and thus sands are washed in order to remove those size fractions that are dangerous. If fine sand is used in some industry, adequate ventilation and suitable protection must be used. (Turkeli, 14-16, 25-29)

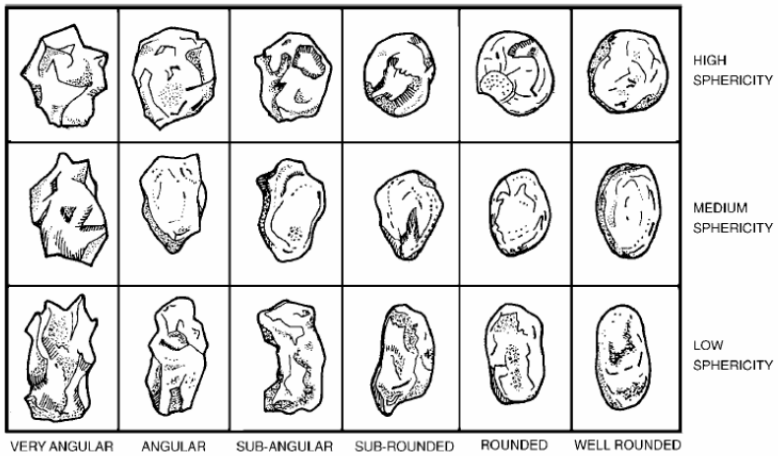


Figure 12.1 *Classification of grain shapes.*

Figure 4. Classification of Sand Grain Shapes (Turkeli, 7)

As a filtering media silica sand is used in municipal and industrial water treatment to remove undissolved solids and bacteria. Filter sand must be uniform in grain size and chemically inert in order to secure effective removal of solids and bacteria. Filter sand should be also hard, well sorted, durable, and high in quartz, and it should not contain grain coatings, clay, silt, organic matter or constituents of iron and manganese. (McLaws 1971, 31)

5.5.2 Diatomite

Diatomite or Diatomaceous Earth is siliceous sedimentary rock and usually very light colored. It consists mostly of silica (85-94%) and aluminium oxide (1-7%), some compounds like iron and titanium oxides and organic matter. The size of the Diatomite varies usually in the range of 50µm to 100µm. Diatomite is very fine-grained and soft and it has very low density and is very finely porous. Other properties of diatomite are low thermal conductivity and high fusion point. Very important property is that diatomite is chemically inert in many liquids. (Antonides, 24.1-24.3)

Diatomite is usually in the form of powder and can cause dust, which could be a problem if not handled and stored properly. Diatomite particles settle relatively quickly in water solutions because they have a specific gravity between 2.0 and 2.3. In order to prevent the settling before the thickener the water flow must be kept high enough. (Logsdon, 238)

The uses of diatomite vary widely from insulators to fillers in paints and coating, plastics and Portland cement. In the industry diatomite can be used as a filter aid to separate solids from the water solutions, or as an absorbent for industrial spills.

The usage of diatomite depends on its physical and chemical properties. Physical properties are such as the size, shape, filtration rate, clarity and absorptive capacity. The specialized applications may need properties such as brightness, whiteness, or abrasiveness. Chemical properties are the content of silica, the form of iron, which is usually the major impurity in diatomite, clay, sand and organics. (Antonides, 24.1-24.3)

5.5.3 Bentonite

Bentonite is a very fine grained clay material that can be found in volcanic ashes and it contains mostly mineral called montmorillonite. Other mineral matters found in bentonite are quartz, feldspar, volcanic glass, gypsum or pyrite and organic matter. Montmorillonite is chemically illustrated as a hydrous aluminium silicate. It contains minor amounts of metals like alkaline and alkaline earth. If any water is available, montmorillonite absorbs it. Water absorption increases the overall volume of the bentonite clay. In the industry the use of bentonite is based on the ability of swelling reaction in water and this is also the most important property of the bentonite clay. The water-to-clay ratio can change, which changes the physical properties of the water and bentonite mixture. The two most common bentonite types are sodium bentonite and calcium bentonite. Sodium bentonite expands more than calcium bentonite in the aqueous solution.

In the industry bentonite and water mixtures can be used for plasticizing, suspending and bonding. As a bonding agent bentonite can be used in various tasks, for example in foundry molding sand and industrial insulation products as a binder. Bentonite suspensions are used in industry. In suspension bentonite particles have disaggregated into colloidal particles, and thus they are corresponded to other colloidal suspensions and have similar physical properties. In suspension bentonite can be used for example as a drilling mud, as fire retardant gel and as part of a float sink or separatory process. Other uses in industry include using bentonite as a clarifying agent. Sediments in the solution are removed from the liquid by filtration or sedimentation, when they have reacted with bentonite. (Cleiyi, Doehler, 272-283)

In water treatment bentonite clay is commonly used as a weighting agent. The dosage that produces rapidly settling flock range from 10 to 50 mg/l. Bentonite increases the turbidity, which accelerates the formation of flocks. (AWWA Staff 2010, 54-55)

6 LABORATORY EXPERIMENTS

Laboratory experiments were conducted in the Norilsk Nickel Harjavalta Oy research laboratory. The first part of the experiments was to examine the precipitation of cobalt and nickel. The other part of the experiments included settling experiments with standard input waters of water treatment plant and some other fractions.

6.1 Precipitation of Nickel and Cobalt as a Function of pH in Carbonate -and Hydroxide Precipitation

The purpose of this experiment was to examine how well cobalt and nickel precipitate from a synthetic solution when the pH is raised stepwise.

The tests were made in the 2l reactor, where the solution was kept at 40˚C and mixed all the time with a mixer. The solution included 1g/L of cobalt (Co), 1g/L of nickel (Ni) and 11g/L of sodium (Na). The pH was raised with sodium carbonate (Na_2CO_3). After certain pH values samples were taken and filtrated with a 5-13µm pore filter in order to remove sediments. The test was repeated first with a hydroxide precipitation (sodium hydroxide, NaOH) test and after that a test starting with carbonate precipitation until the pH 10 and ending with hydroxide precipitation until the pH 13.

The samples were diluted with dilution factor 20 and they were analysed with ICP3 analyzer.

The experimental procedure plan was designed in order to show the tests that have been done. Below is a table of precipitation experiments that included the addition of sodium carbonate and sodium hydroxide and sampling at certain pH values are expressed in the table. Experiments were carbonate precipitation (A1), hydroxide precipitation (A2), and carbonate –and hydroxide precipitation (A3)

Table 1. Precipitation of Cobalt and Nickel

	Carbonate precipitation (A1)	Hydroxide precipitation (A2)	Carbonate- and hydroxide precipitation (A3)
Samples taken at pH	7	7	Carbonate p.
	8	8	7
	8,5	9	8
	9	9,5	8,75
	9,25	10	9
	9,5	10,25	9,5
	9,75	10,5	10
	10	10,75	Hydroxide p.
		11	10,25
		11,5	10,5
		12	10,75
		12,5	11
		13	11,25
			11,5
			12
			12,5
			13

Figure 5. The Reactor and a Water Bath Used in the Experiments

6.2 Settling Experiments

The purpose of these tests was to examine the effectiveness of removing cobalt and nickel from the solution by using alternative settling agents in the processes. In order to perform the experiments water samples were taken from the water treatment plant.

6.2.1 Experiments with New Fractions

The fractions that could possibly be directed to the water treatment process were NiPK1, NiPK3 and CuIX fractions and they were all tested separately. The tests were made in the reactor at 40˚C and with constant mixing. First fractions were precipitated with sodium carbonate (Na_2CO_3) until the pH was 9.5. The precipitated solution was filtrated with 2µm pore size paper filtration and Büchner funnel in order to remove the sediments. The filtrated solution was divided into 5 different sections and these sections were precipitated separately with sodium hydroxide (NaOH) until the pH was 10.5. In all the experiments same Na_2CO_3 (196g/l) and NaOH (200g/l) were used. Alternative settling agents were added to the sections separately during sodium hydroxide precipitation. The settling agents were ferric sulphate (Fennoferri 322), diatomite and silica sand. Diatomite and silica sand had two different dosages.

Settling experiments were conducted in a 100ml graduated glass. Tested solution with settling agent and 1,5g/m^3 flocculent (Flopam FO4125SH) were mixed carefully. The settlement time was 15 minutes and the “height” of the settlement was verified after certain time periods. After 15 minutes an unfiltered sample was taken from the surface water in order to copy the circumstances in the water treatment process thickener and its overflow water.

The samples were diluted with a dilution factor 2 and analyzed in the laboratory with ICP3 analyzer.

The experimental procedure plan below shows the experiments conducted. Experiments were CuIX precipitation and settling (B1), NiPK1 precipitation and settling (B2) and NiPK3 precipitation and settling (B3). All these fractions had the same experimental procedure with same weighting agents.

Table 2. Settling Experiments New Fractions

Settling experiments	Settling agent dosages				
CuIX (B1)	Ferric sulphate 0,5ml/L	Diatomite 1 100mg/L	Diatomite 2 250mg/L	Silica sand 1 100mg/L	Silica sand 2 250mg/L
NiPK1 (B2)					
NiPK3 (B3)					

The dosages were calculated based on the flow of incoming water flows to the water treatment precipitation reactor RE 3701, which was estimated to be totally 100m^3/h. The dosages are for ferric sulphate 50l/h, and for diatomite and silica sand 10kg/h and 25kg/h.

6.2.2 Water Treatment Inputs and New Fractions Together

The average input flows entering the water treatment precipitation reactor RE3701 were investigated. A table and a figure with all the inputs based on their percentual amounts were made by using Norilsk Nickel Harjavalta Oy chart of incoming water flows. In normal conditions the acidic and alkaline waters from calcium extraction process enter the precipitation reactor separately but the conditions have temporarily changed and the flows enter the precipitation reactor as one flow. Due to this some precipitation of the soluble metals may occur already while being directed to the water treatment process.

Table 3. Standard Input Waters

Input waters	Average feed flow, m^3/h
LS 283	25,6
PS 323 (Calcium Extraction)	14,4
VS 3851 (Process Waters from Chemical Plant)	40,7
PVA (Process water pool)	4,0
RVA (Rainwater pool)	9,7
JTS 3651 (Waste Water Expansion Tank)	2,3
Sodium hydroxide	0,3
Total	97

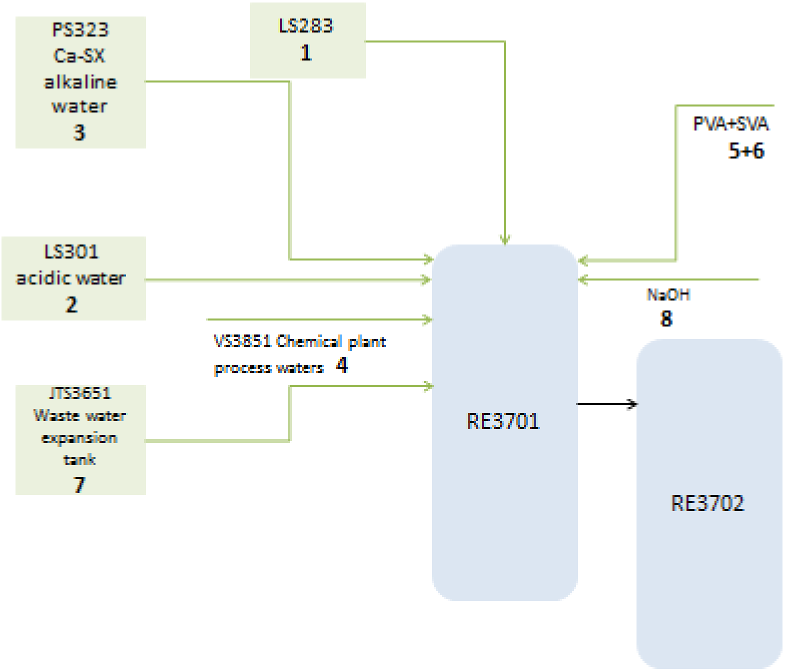


Figure 6. The Input Waters Entering the Precipitation Reactor RE 3701

The first settling experiment was conducted with the standard input waters entering the precipitation reactor RE 3701. The mixture was made from the water samples taken from the incoming water flows. The amount of each input water sample was based on the percentage share from the total input water flow (100m³/h). The mixture of the sample waters was totally 1,8L.

Table 4. The Relative Amounts of Standard Input Waters

Income water sample	%	ml/1,8L
LS 283	27	490
PS 323	15,3	270
VS 3851	43	770
Process water pool	4,2	76
Rainwater pool	10,2	180
JTS 3651	2,4	43

The test was made in a 2l reactor; the mixture was added to the reactor with constant mixing and a temperature of 43˚C. In order to conduct the settling experiments, 250ml of the solution was taken from the mixture at the time and alternative weighting agent was added and then mixed carefully.

The rest of the experiments included also the addition of fractions NiPK1, NiPK3 and CuIX. These fractions were first precipitated with sodium carbonate until the pH was 9.5 and then filtrated in order remove the sediments. Then the filtrated fractions were added to the mixture of incoming waters. If the pH was under 10.5, sodium hydroxide was added to the final mixture the required amount.

The amounts of the fractions in the mixture were calculated based on their average flows. The fractions do not enter to the water treatment precipitation reactor at the moment. The calculations were based on the assumption that they would enter the precipitation reactor. The percentages were based on the total flow of incoming waters and on the assumption that the fractions would enter there too. The amounts of them in the mixture were then calculated based on the percentages of the fractions.

Table 5.The Relative Amounts of New Fractions

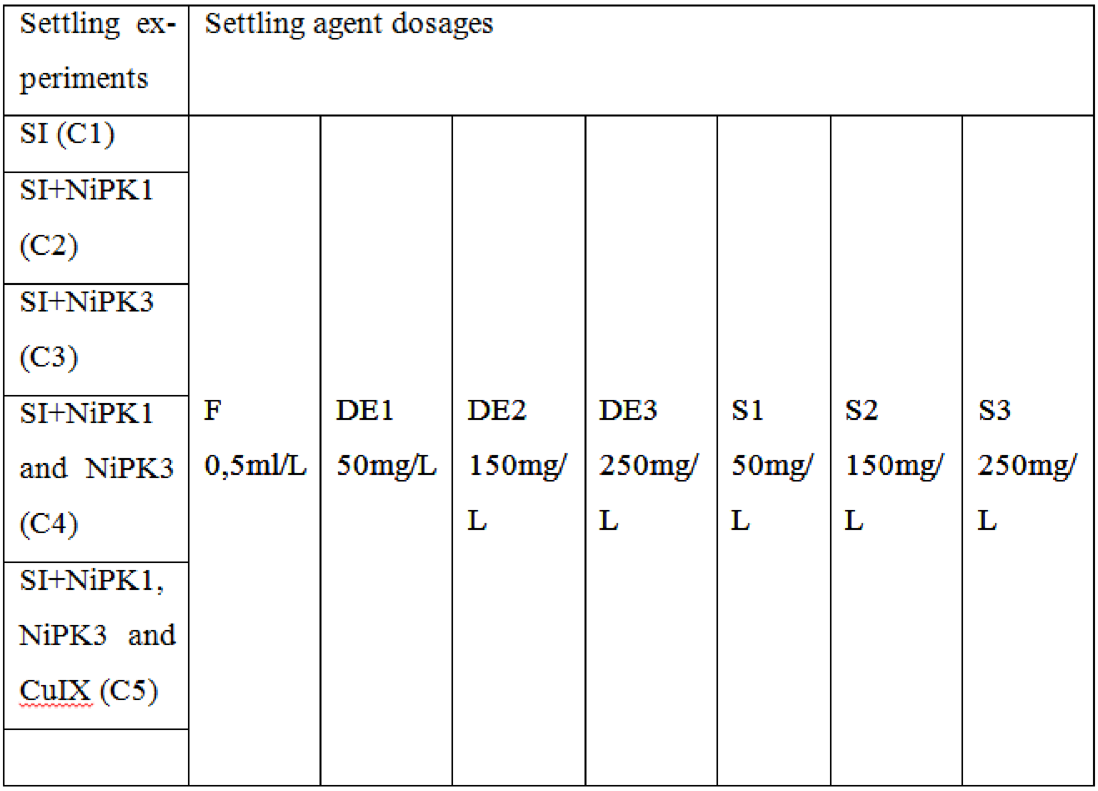
Fraction	Average flow, m³/h	%	ml/1,8L
NiPK1	4,80	4,1	73
NiPK3	2,70	2,8	50
CuIX	3,0	3,0	no experiment
NiPK1+NiPK3	7,5	NiPK1 64%, NiPK3 36%	120
NiPK1, NiPK3 and CuIX	10,5	NiPK1 46%, NiPK3 26%, CuIX 28%	180

The sample was poured to a 100ml graduated glass and 1,5g/m³ flocculent was added and then mixed carefully. The settlement time was 15 minutes and the height of settlement was verified at certain time periods. After 15 minutes a sample was taken from the surface water in order to copy the circumstances in the water treatment process thickener and its overflow water.

The samples were diluted with a dilution factor 2 and analyzed in the laboratory with ICP3 analyzer.

The experimental procedure plan was made in order to show the conducted experiments. The experiments were Standard Inputs (SI) settling experiment (C1), SI and NiPK1 settling experiment (C2), SI and NiPK3 settling experiment (C3), SI, NiPK1 and NiPK3 settling experiment (C4), and SI,NiPK1, NiPK3 and CuIX settling experiment (C5) All the experiments were conducted in the same way; expect the experiment of Standard inputs because it didn't need to be precipitated.

Table 6. Settling Experiments SI, NiPK1, NiPK3 and CuIX



Settling experiments	Settling agent dosages						
SI (C1)	F 0,5ml/L	DE1 50mg/L	DE2 150mg/L	DE3 250mg/L	S1 50mg/L	S2 150mg/L	S3 250mg/L
SI+NiPK1 (C2)							
SI+NiPK3 (C3)							
SI+NiPK1 and NiPK3 (C4)							
SI+NiPK1, NiPK3 and CuIX (C5)							

The letters in the table stood for weighting agents; F for Ferric sulphate, DE for Diatomaceous Earth and S for Silica sand. The dosages of the weighting agents were based on the total input flow of the water treatment precipitation reactor RE 7301, which was 100m³/h. The dosages were for diatomite and silica sand DE1 and S1 5kg/h, DE2 and S2 15kg/h and DE3 and S3 25kg/h.

6.2.3 Water Treatment Inputs and New Fractions Together Extended Time

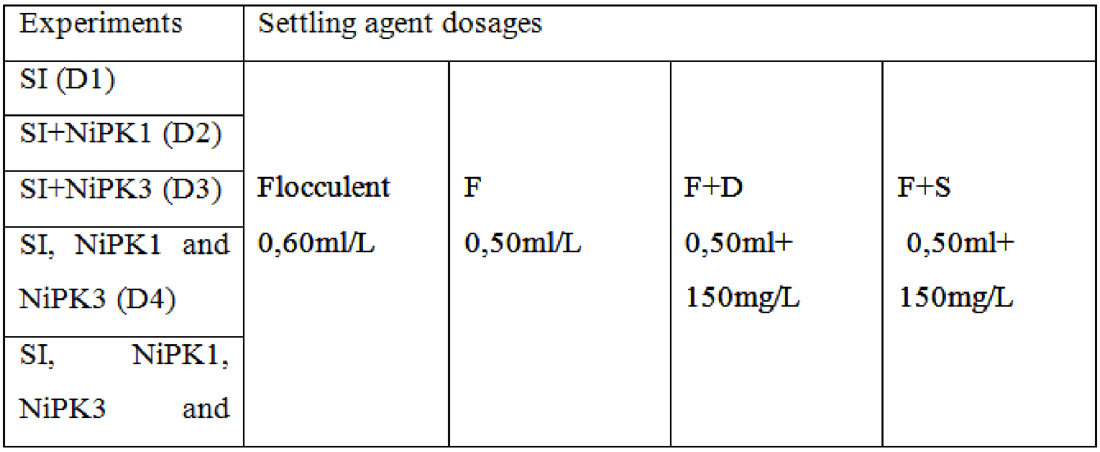
Some more experiments were decided to be conducted in order to discover whether too short reaction time of the mixture and ferric sulphate affected the flocculation and settling in previous experiments.

The tests were conducted basically in the same way as before in the settling experiments. After the 1,8L initial solution was prepared, the pH was raised with sodium hydroxide until it was 10.5. Then the solution was divided into four different sections. First settling experiment was conducted only with flocculent in order to examine the effectiveness of the settling agents compared only to the usage of flocculent in the settling process. The second experiment included the 30 minutes reaction time of the mixture and ferric sulphate in the reactor at the temperature of 43˚C with constant mixing. After 30 minutes the settling experiment was conducted as before; 15 minutes in the 100 graduated glass with 1,5g/m³ of flocculent. The third and fourth experiments included 30 minutes reaction time of ferric sulphate and the mixture together with settling agents sand and diatomite, and the 15 minutes settling.

The experiments included the same amounts of water treatment plant incoming water flows than in the previous experiments. Also the amounts of NiPK1, NiPK3 and CuIX fractions were the same as before.

The experimental procedure plan was made. The experiments were Standard Inputs (SI) settling experiment (D1), SI and NiPK1 settling experiment (D2), SI and NiPK3 settling experiment (D3), SI, NiPK1 and NiPK3 settling experiment (D4) and SI, NiPK1, NiPK3 and CuIX settling experiment (D5).

Table 7. Settling Experiments SI, NiPK1, NiPK3 and CuIX 30min Reaction Time



Experiments	Settling agent dosages			
SI (D1)	**Flocculent** 0,60ml/L	F 0,50ml/L	F+D 0,50ml+ 150mg/L	F+S 0,50ml+ 150mg/L
SI+NiPK1 (D2)				
SI+NiPK3 (D3)				
SI, NiPK1 and NiPK3 (D4)				
SI, NiPK1, NiPK3 and				

The letters in the table stood for weighting agents; F for Ferric sulphate, D for Diatomaceous Earth and S for Silica sand. The dosages of the settling agents were for ferric sulphate 50l/h, and for diatomite and sand 15kg/h based on the total incoming water flows to the water treatment plant.

6.3 Silica Sand as a Settling Agent in Production Scale

One part of the thesis was to investigate whether the settling agents could be utilized as a part of water treatment process. The aim was to use one or two settling agents in a production scale as pilot study. The results would have indicated whether the presence of a settling agent could improve the sedimentation process and thus decrease the concentration of nickel and cobalt in the water discharged to the river.

The plan was to use silica sand with different dosages, which were 5kg/h, 15kg/h, and 25kg/h, in the water treatment process. The sand was distributed to the pipeline between the precipitation reactors RE 3702 and RE 3703 by using a dosing feeder. The plan was to feed sand for five days per one dosage amount. The experiment was carried out with the help of process workers because the sand feed was supposed to be constant. The dosing feeder was designed to contain about 70kg of sand at a time and the mass of one sand bag was 40kg. Extra samples were taken daily in order to monitor whether the sand feed would affect to the effectiveness of cobalt and nickel removal.

The calibration of the sand dosing feeder was done by weighting the sand that was collected from the feeder during five minutes time and then converting that to the feed of one hour.

Figure 7. Sand Dosing Feeder

7 RESULTS

7.1 Results from the Hydroxide – and Carbonate Precipitations

In the carbonate and hydroxide precipitation the solubilities of nickel and cobalt at different pH were measured. At certain pH values a sample was taken and filtrated. The results were documented in the field book, Appendix 1.

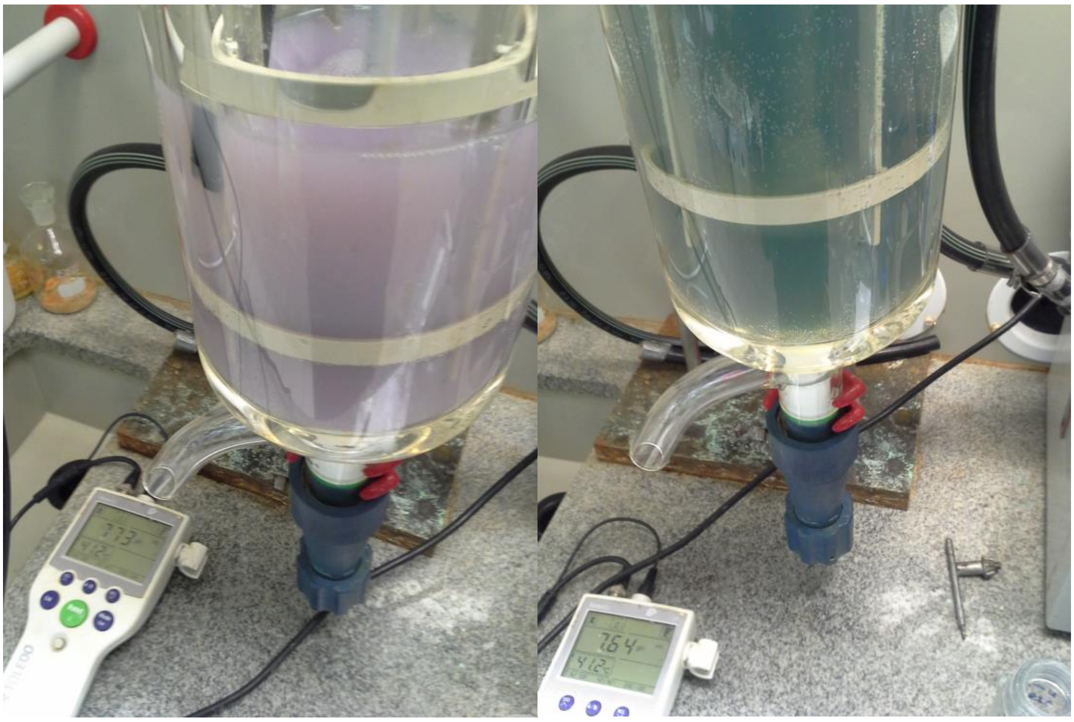


Figure 8. The precipitation of nickel and cobalt solution a) carbonate precipitation on the left side b) hydroxide precipitation on the right side

The precipitation occurred at different pH values in carbonate and hydroxide precipitations as can be seen from the pictures where the precipitation has started in the Figure 8a) but not in the 8b) even if the pH values are almost the same.

The solubility tables seen before (Figure 1, Figure 2) showed the theoretical solubilities of cobalt and nickel with carbonate and hydroxide precipitation. During the carbonate precipitation experiment the sedimentation of the solution containing nickel and cobalt started around pH 7. During the hydroxide precipitation experiment the sedimentation of the solution started around pH 8.

Figures 9, 10, and 11 illustrate the precipitation of nickel and cobalt in carbonate -, hydroxide -, and carbonate –and hydroxide precipitations.

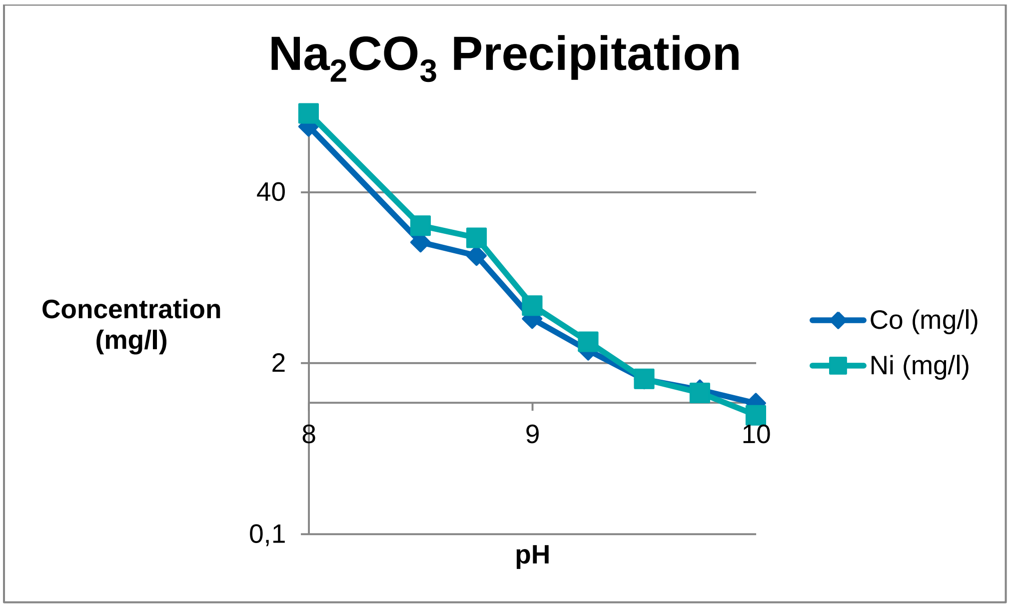


Figure 9. Na_2CO_3 Precipitation 11.3.2014

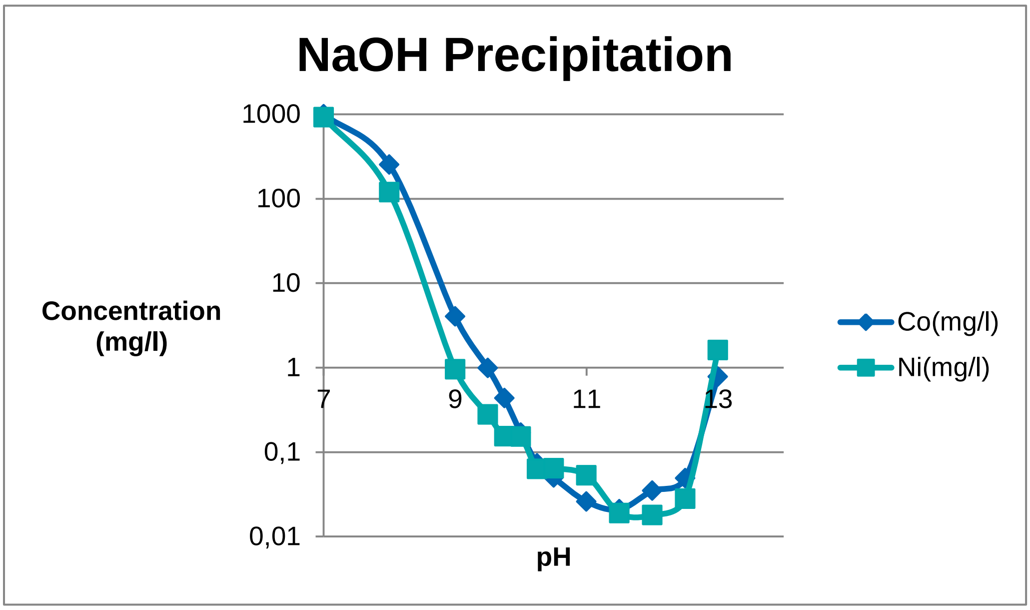


Figure 10. NaOH Precipitation 12.3.2014

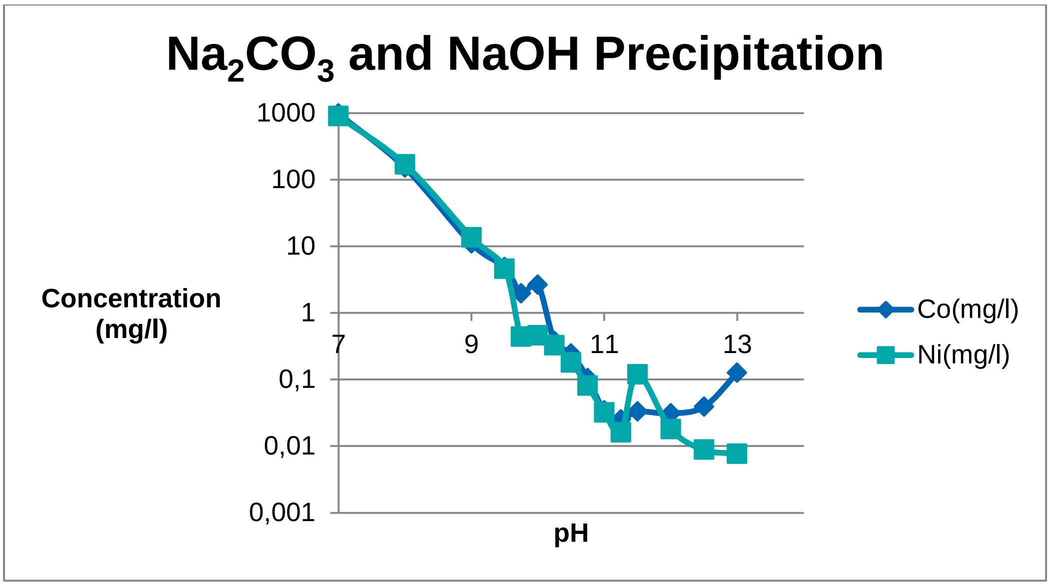


Figure 11. Na_2CO_3 and NaOH Precipitation 14.3.2014

The initial concentrations of nickel and cobalt (1 g/L) were not shown in the figures because the concentrations were high and the decrease in the concentration was effective. From the figures can be seen that the hydroxide precipitation was more effective than carbonate precipitation. In the hydroxide precipitation cobalt and nickel dissolved back at alkaline pH, this can be seen in the increase of the concentrations.

To compare the results of the precipitation experiments with the Figures 1 and 2 the concentrations of nickel and cobalt should be converted to the unit mol/L using the equation:

$$n\ (mol) = \frac{m\ (g)}{M\ (\frac{g}{mol})} \tag{2}$$

The molar masses of cobalt and nickel are: Co=58,93mol/kg and Ni= 58,69mol/kg.

Table 8. Concentrations of Cobalt and Nickel Converted to mol/L

	pH	Co (mg/L)	Co (mol/L)	Ni (mg/L)	Ni (mol/L)
Na_2CO_3	8	126,2	2,1 E-04	159,2	2,7 E-04
	9	4,35	7,4 E-05	5,49	9,4 E-05
	10	0,99	1,7 E-05	0,80	1,4 E-05
NaOH	8	252,7	4,3 E-04	119,4	2,0 E-04
	9	4,02	6,8 E-05	0,96	1,6 E-05
	10	0,17	2,9 E-06	0,15	2,6 E-06
	11	0,021	3,6 E-07	0,019	3,2 E-07

From the Table 8 and Figures 1 and 2 can be seen that the solubilities of cobalt and nickel were comparable. The Figure 1 illustrated the solubilities of cobalt and nickel in carbonate precipitation and it can be seen that the concentrations of cobalt and nickel were close to 1E-05 mol/L when the pH was about 7. In the Table 8 the concentrations were close to 2E-04 mol/L when the pH was about 8. The Figure 2 illustrated the solubilities of cobalt and nickel in hydroxide precipitation and it can be seen that the concentrations of cobalt and nickel were close to 1E-03 when the pH was about 8 and close to 1E-05 when the pH was about 9. In the Table 8 the concentrations of nickel and cobalt were close to 4E-04 and 2E-04 at pH 8 and close to 7E-05 and 2E-05 at pH 9. Comparison between the Figures 1 and 2, and the Table 8 illustrated that there was more cobalt and nickel soluble in the solution in carbonate precipitation experiment than in the Figure 1 and that there was less cobalt and nickel soluble in hydroxide precipitation experiments than in the Figure 2.

7.2 Results from the Settling Experiments

The results of the settling experiments were documented in the field books Appendix 2, 3, and 4). Results from the settling experiments include:

- the volume of the sedimentation bed in ml as a function of time shown in figures
- the concentration of cobalt and nickel
- the observations during the settling experiments
- some of the results include the height sedimentation bed in the bottom (ml)

The settling experiments were all conducted similarly. The height of the settling flocks (ml) was quite high in all the experiments, which in turn showed that the formation of flocks and their settling to the bottom was not really effective.

7.2.1 Results from New Fractions

Figures 12, 13, 14 illustrate the settling of New Fractions: CuIX, NiPK3 and NiPK1 as a function of settling time. In the tables the letters stood for weighting agents; F for Ferric sulphate, DE for Diatomaceous Earth and S for Silica sand. The Tables 9,10 and 11 illustrate the concentrations of new fractions at the start of the experiment , after filtration and after the settling experiment with different settling agents.

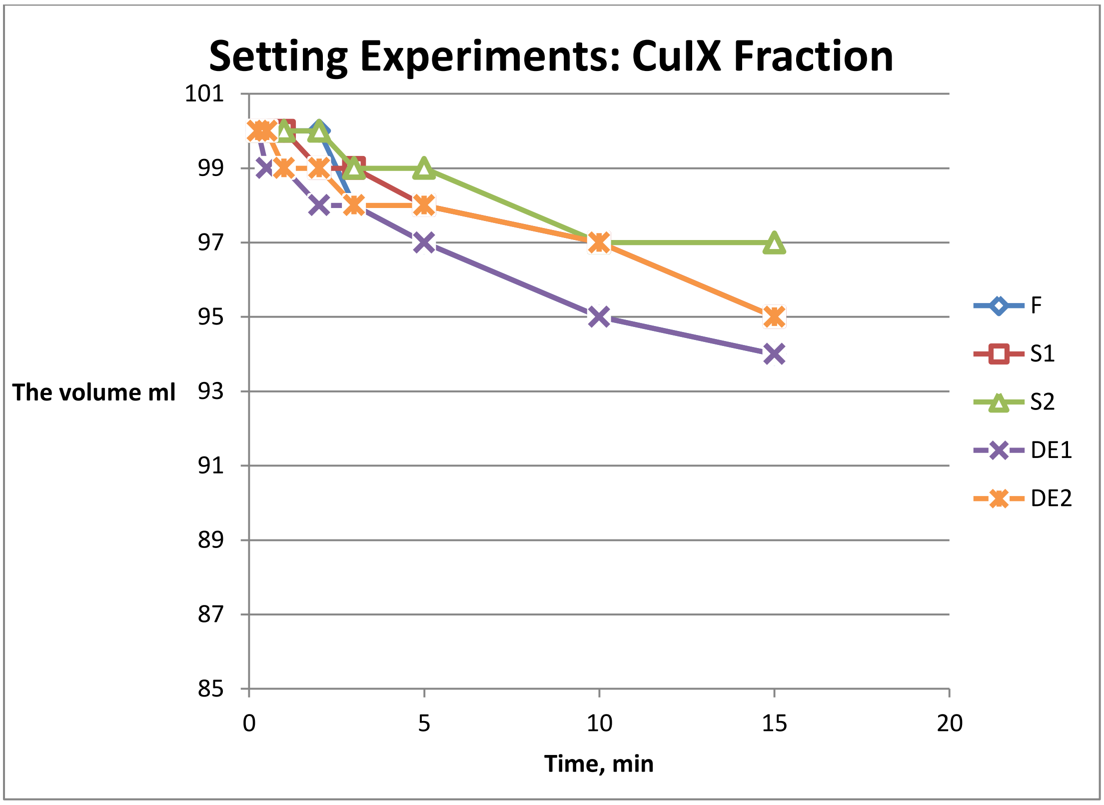


Figure 12. The Settling of CuIX Fraction 17.3.2014

Table 9. Concentrations of Cobalt and Nickel after Settling Experiment CuIX Fraction

	Original	Filtrated	F	S1	S2	DE1	DE2
Co (mg/l)	53,18	1,415	0,534		0,475	1,821	2,079
Ni (mg/l)	0,359	0,055	1,661	2,393	1,36	0,045	0,0479

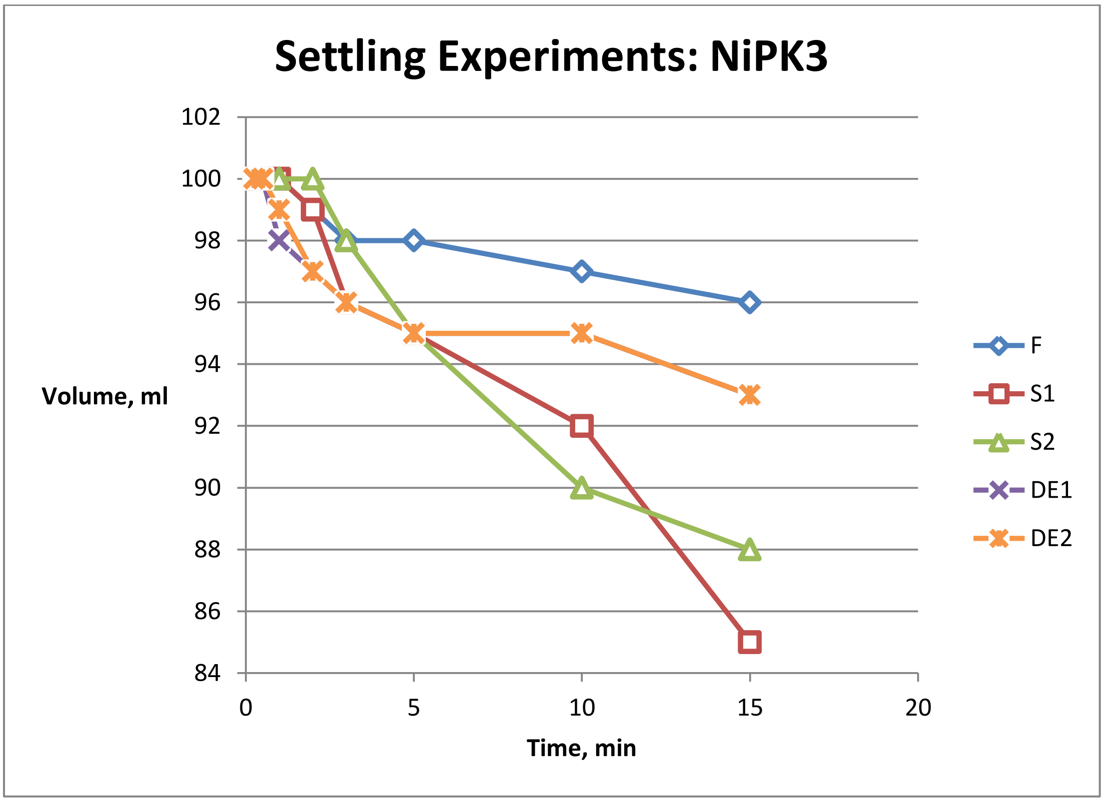


Figure 13. The Settling of NiPK3 Fraction 20.3.2014

Table 10. Concentrations of Cobalt and Nickel after Settling Experiment NiPK3 Fraction

	Original	Filtrated	F	S1	S2	DE1	DE2
Co (mg/l)	25,12	0,496	0,133	0,195	1,538	0,275	0,275
Ni (mg/l)	0,319	0,039	0,041	0,256	4,846	0,631	0,536

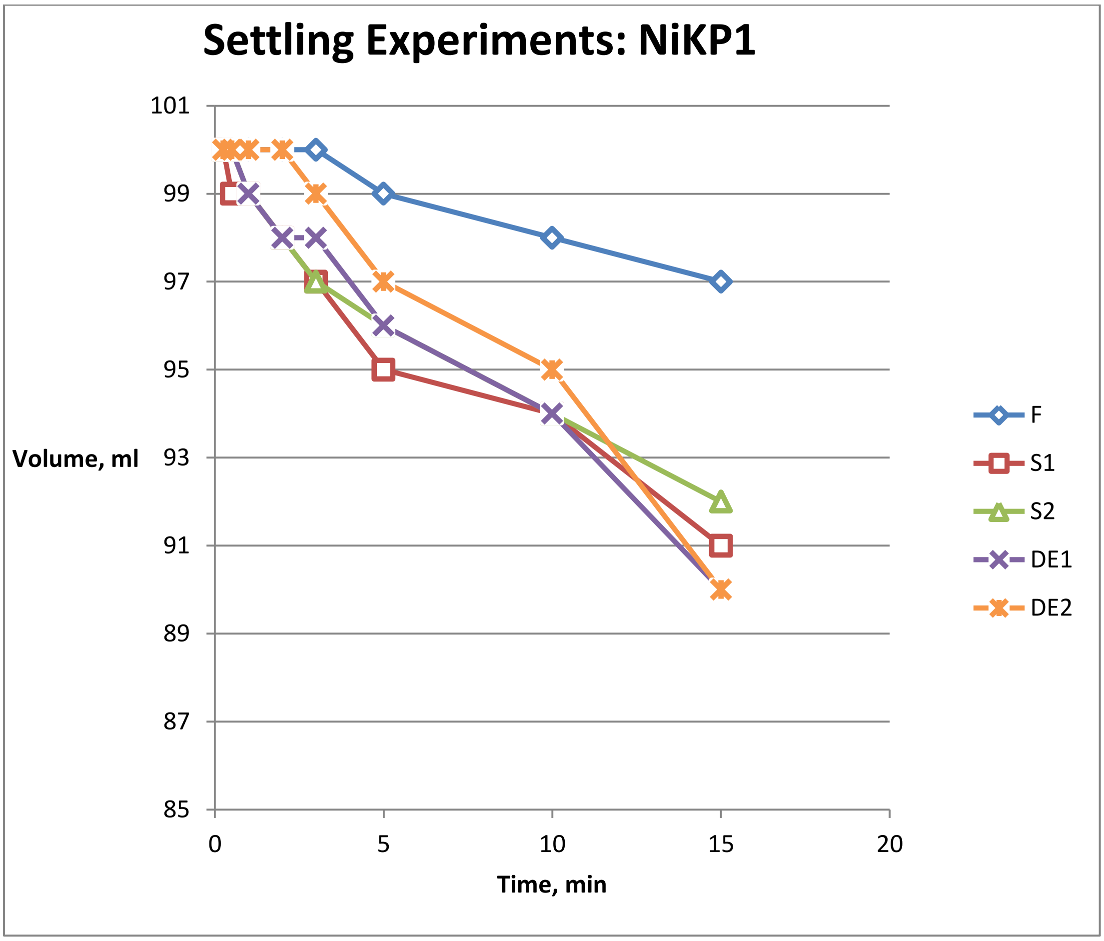


Figure 14. The Settling of NiPK1 Fraction 24.3.2014

Table 11. Concentrations of Cobalt and Nickel after Settling Experiment NiPK1 Fraction

	Original	Filtrated	F	S1	S2	DE1	DE2
Co (mg/l)	29,95	7,207		0,755	0,601		1,345
Ni (mg/l)	0,508	0,283	0,064	0,004	0,004		0,543

From the figures can be seen that the settlement of the sediments was not effective because the height of the flocks was quite high after 15min time. There were not big differences between the settling agents. From the figures can be seen that in most of the experiments ferric sulphate settled the poorest. The results in the Tables 9,10 and 11 indicated that the concentrations of nickel and cobalt varied only slightly with different settling agents. There were problems in the analysis of NiPK1 and CuIX and thus some of the results were left away.

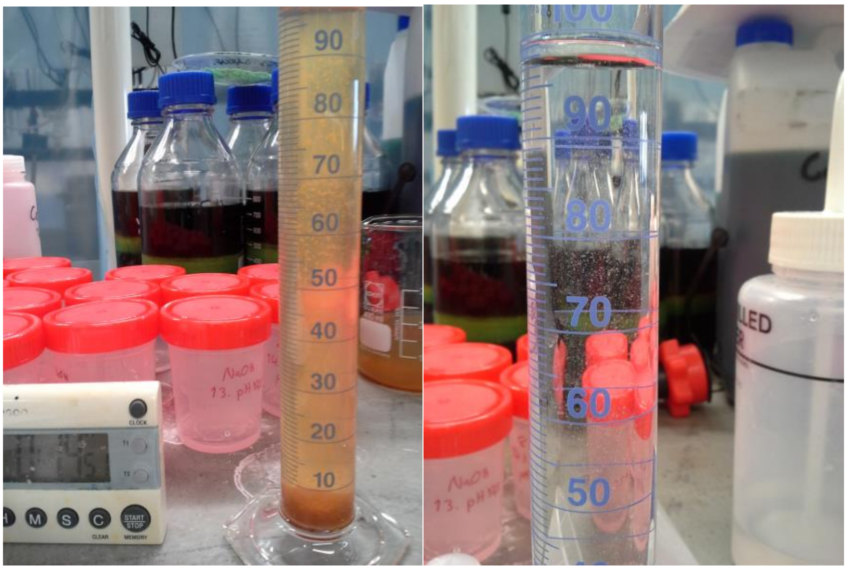


Figure 15. a) Ferric Sulphate on the left side b) Silica Sand on the right side used as settling agents

From the Figure 15 can be seen the difference between the settling agents. Ferric sulphate as a settling agent created large and orange flocks whereas silica sand and diatomite very small flocks.

7.2.2 Results from Water Treatment Inputs and New Fractions

Figures 16, 17, 18, 19 and 20 illustrate the settling of standard input waters and standard input waters with NiPK1, NiPK3 and CuIX fractions as a function of time. The Tables 12, 13, 14, 15 and 16 illustrate the original concentrations of nickel and cobalt and concentrations gained after the settling experiments.

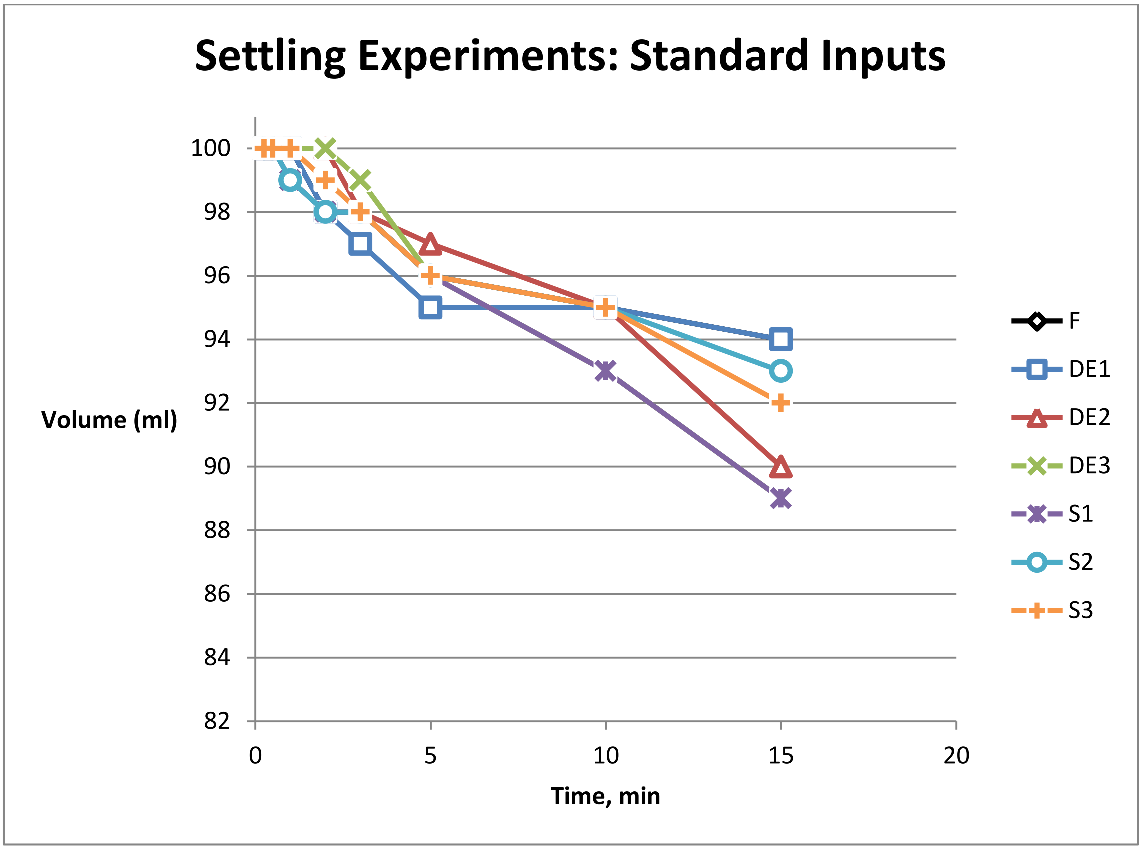


Figure 16. The Settling of Standard Input Waters 27.3.

Table 12. Concentrations of Cobalt and Nickel after Settling Experiment Standard Input Waters

	Original	F	DE1	DE2	DE3	S1	S2	S3
Co (mg/l)	5,69	0,182	0,647	0,568	0,293	0,853	2,058	1,14
Ni (mg/l)	6,17	0,136	0,735	0,662	0,296	1,018	1,288	2,413

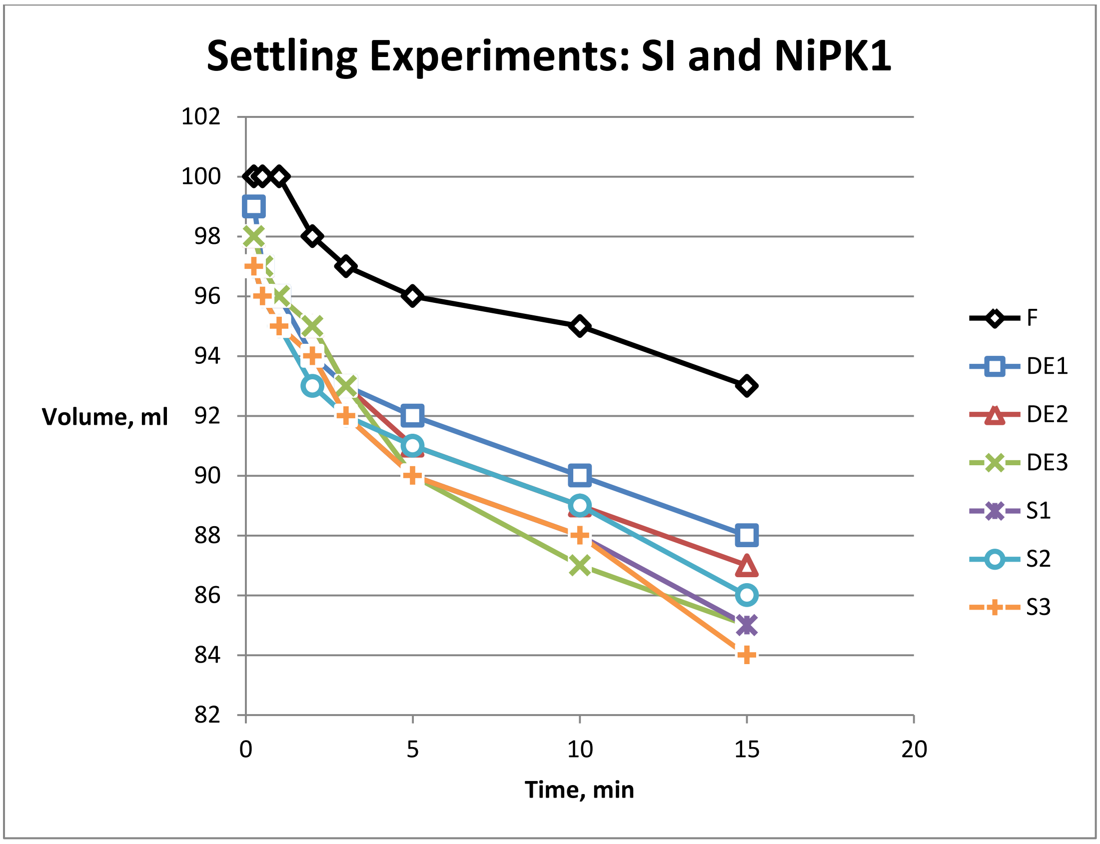


Figure 17. The Settling of SI and NiPK1 2.4.2014

Table 13. Concentrations of Cobalt and Nickel after Settling Experiment SI and NiPK1

	Original	F	DE1	DE2	DE3	S1	S2	S3
Co (mg/l)	0,45	0,166	0,149	0,151	0,141	0,138	0,147	0,168
Ni (mg/l)	10,94	0,924	1,38	1,397	1,527	1,525	1,628	1,812

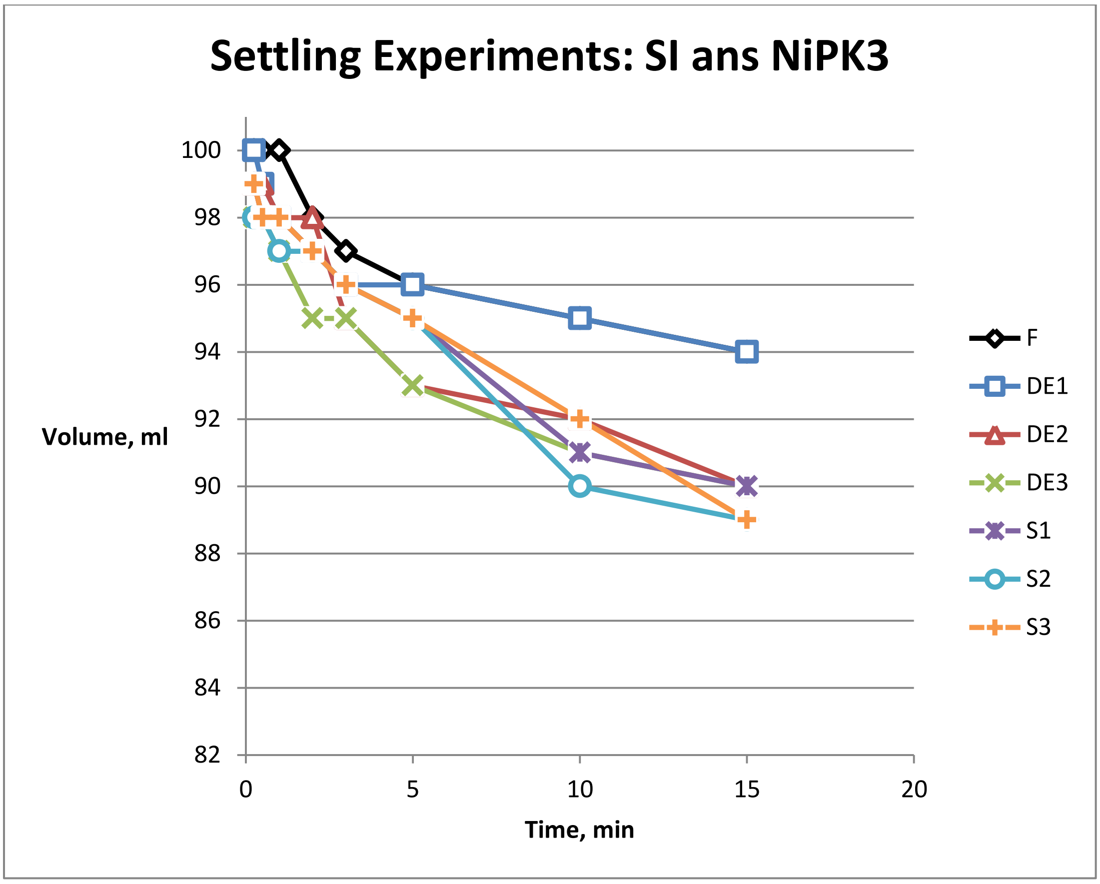


Figure 18. The Settling of SI and NiPK3 31.3.2014

Table 14. Concentrations of Cobalt and Nickel after Settling Experiment SI and NiPK3

	Original	F	DE1	DE2	DE3	S1	S2	S3
Co (mg/l)	3,09	0,176	0,359	0,265	0,271	0,442	0,568	0,521
Ni (mg/l)	9,27	0,422	5,293	3,793	4,106	8,482	10,46	10,34

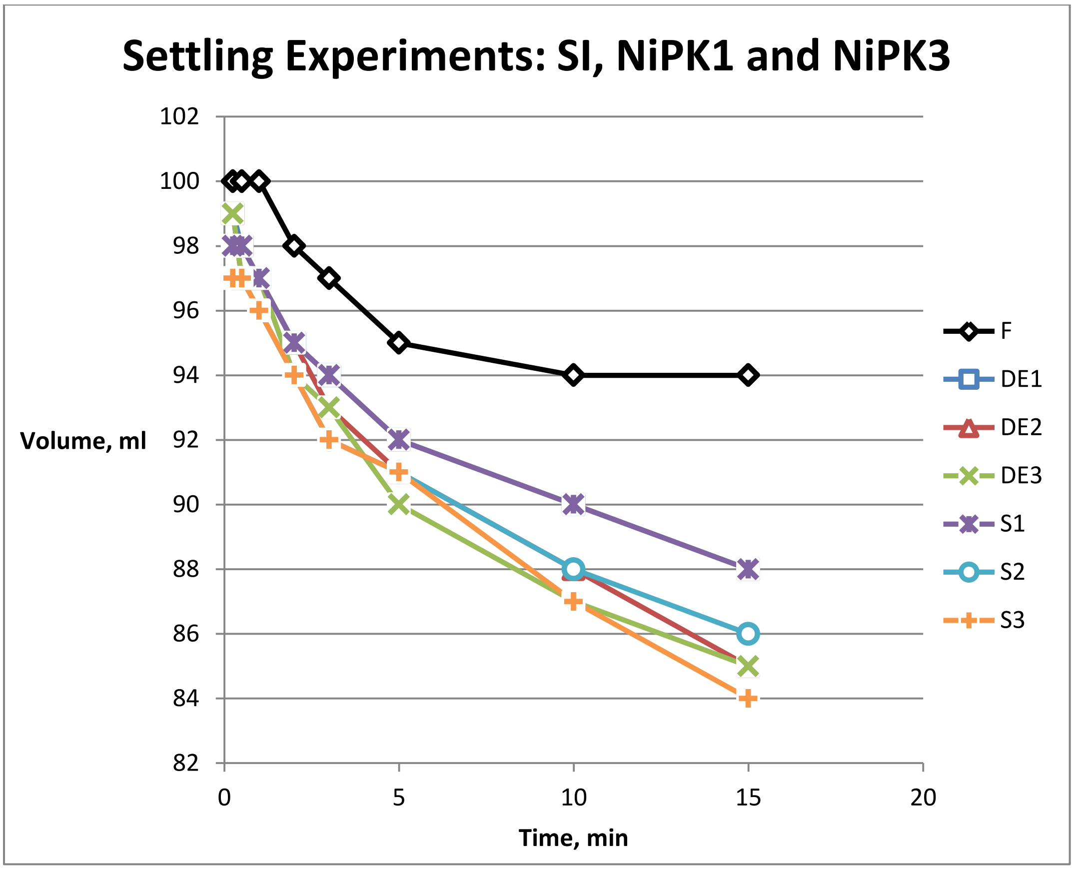


Figure 19. The Settling of SI, NiPK1 and NiPK3 3.4.2014

Table 15. Concentrations of Cobalt and Nickel after Settling Experiment SI, NiPK1 and NiPK3

	Original	F	DE1	DE2	DE3	S1	S2	S3
Co (mg/l)	1,70	0,319	0,25	0,233	0,256	0,372	0,348	0,295
Ni (mg/l)	9,84	4,626	4,798	4,401	5,433	9,16	7,913	6,851

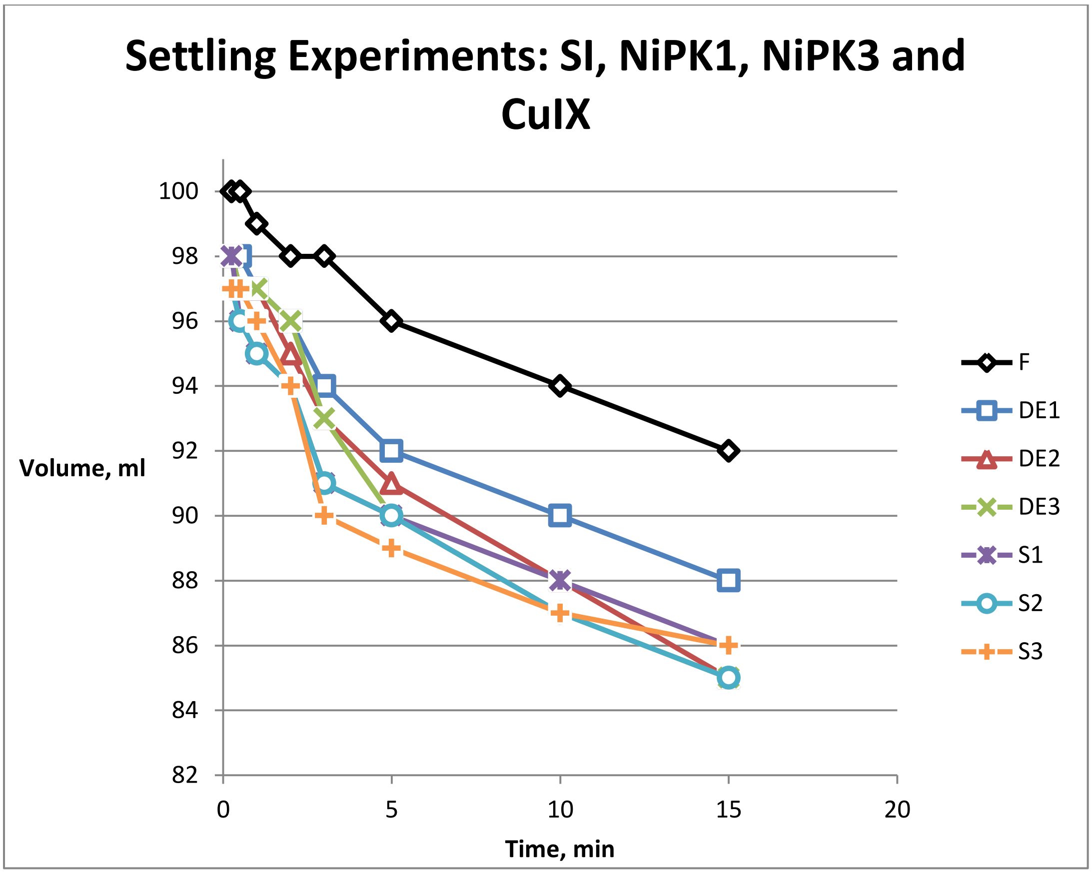


Figure 20. The Settling of SI, NiPK1, NiPK3 and CuiX 4.4.2014

Table 16. Concentrations of Cobalt and Nickel after Settling Experiment SI, NiPK1, NiPK3 and CuIX

	Original	F	DE1	DE2	DE3	S1	S2	S3
Co (mg/l)	0,56	0,36	0,227	0,249	0,219	0,259	0,292	0,311
Ni (mg/l)	10,57	5,82	4,441	5,413	4,575	5,832	6,492	7,489

From the figures can be seen that the settling process was not very effective because the height of the sedimentation was quite high in all experiments. There was a bed of sediments in all the experiments but the small and light flocks did not settle completely and thus the excess water was turbid. From the figures can also be seen that ferric sulphate as a settling agent was the poorest and during the experiments was seen that the flocks formed during the ferric sulphate settling were large but weakly settleable. The results in the tables 12, 13, 14, 15 and 16 indicated that the best results were gained in most cases with diatomite or with ferric sulphate. The poorest results were gained with sand. Concentration of nickel and cobalt varied little when the dosages of diatomite and sand were changed.

7.2.3 Results from Water Treatment Inputs and New Fractions extended time

The figures 21, 22, 23, 24, and 25 illustrate the settling of standard input water flows, NiPK1, NIPK3 and CuIX with the 30 min reaction time with ferric sulphate. The Tables 17, 18, 19, 20 and 21 illustrate the original concentrations of nickel and cobalt and the concentrations after the settling experiments.

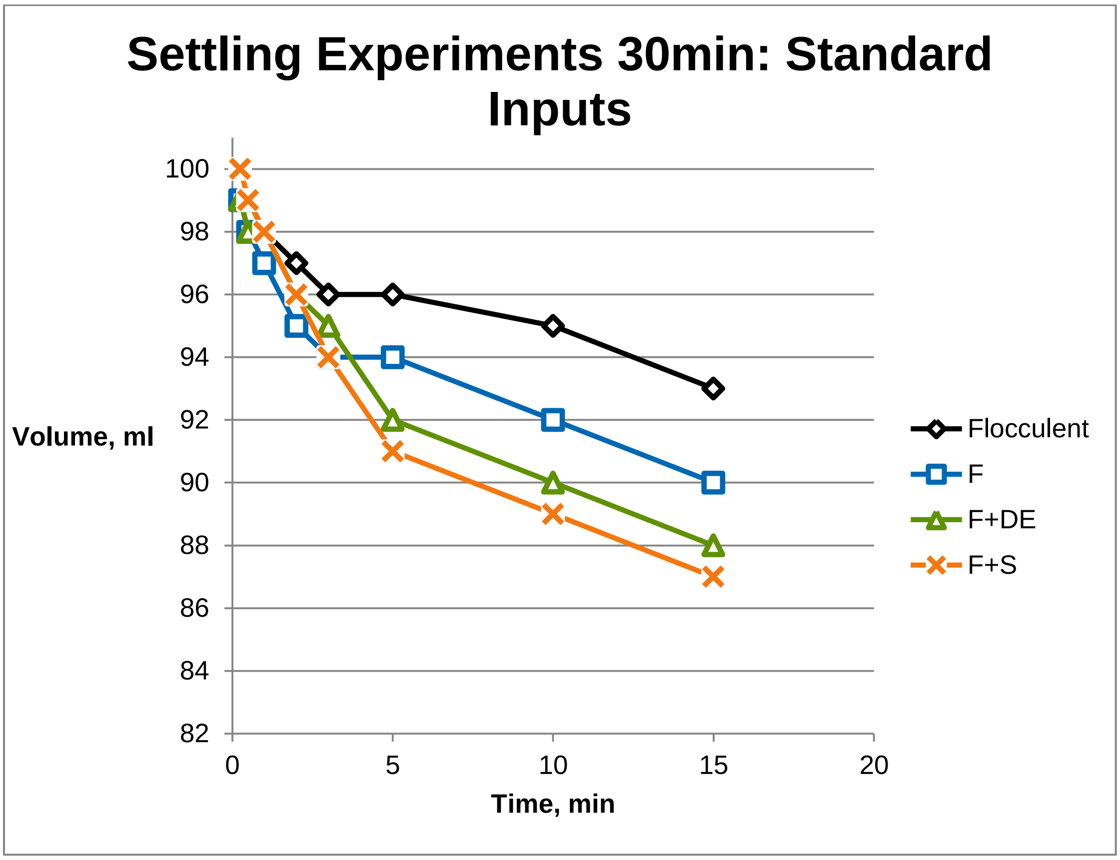


Figure 21. The Settling of Standard Input Waters 30 min Reaction Time 8.4.2014

Table 17. Concentrations of Cobalt and Nickel after Settling Experiment Standard Input Waters 30min Reaction Time

	Flocculent	F	F+DE	F+S	Original
Co (mg/l)	0,199	0,1815	0,1688	0,2045	0,621
Ni (mg/l)	8,772	13,922	13,614	19,899	85,201

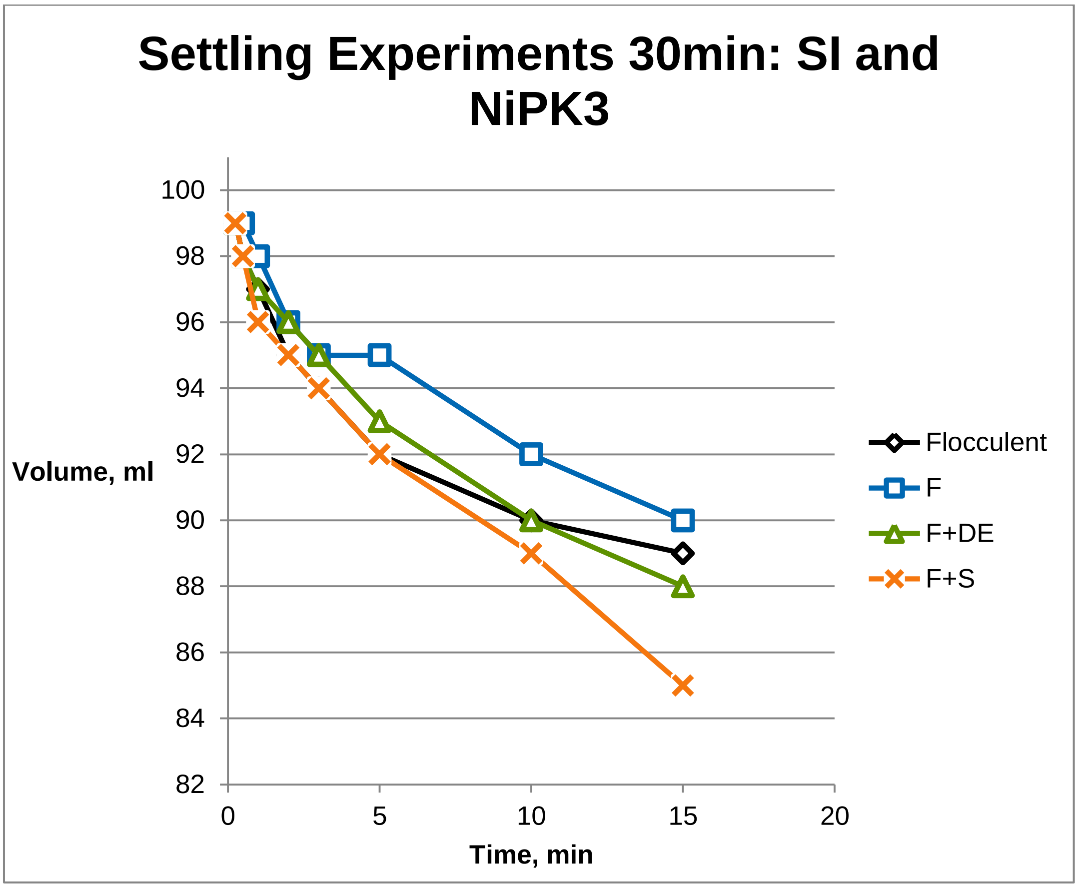


Figure 22. The Settling of SI and NiPK3 30 min Reaction Time 15.4.2014

Table 18. Concentrations of Cobalt and Nickel after Settling Experiment SI and NiPK3 30min Reaction Time

	Flocculent	F	F+DE	F+S	Original
Co (mg/l)	0,195	0,228	0,162	0,179	0,405
Ni (mg/l)	13,785	24,738	12,414	14,582	31,214

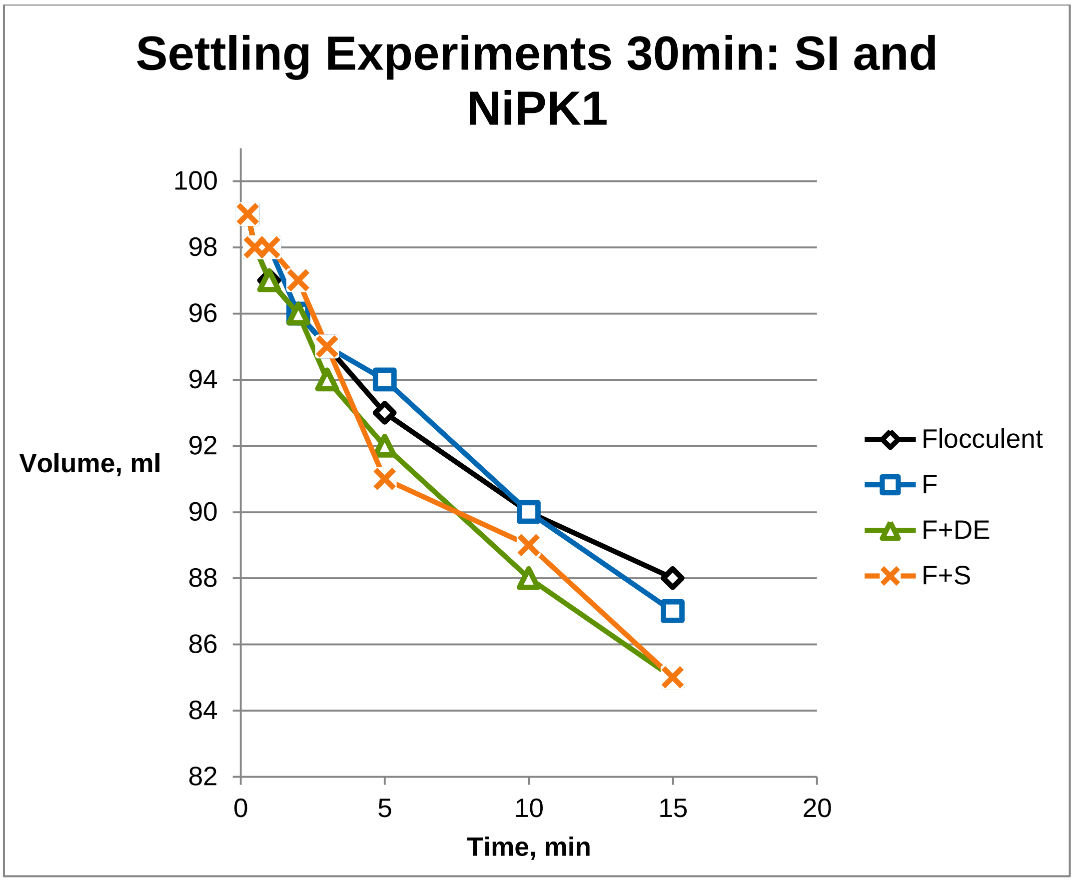


Figure 23. The Settling of SI and NiPK1 30min Reaction Time 16.4.2014

Table 19. Concentrations of Cobalt and Nickel after Settling Experiment SI and NiPK1 30min Reaction Time

	Flocculent	F	F+DE	F+S	Original
Co (mg/l)	0,186	0,109	0,0818	0,117	0,551
Ni (mg/l)	8,597	10,11	6,507	12,259	32,109

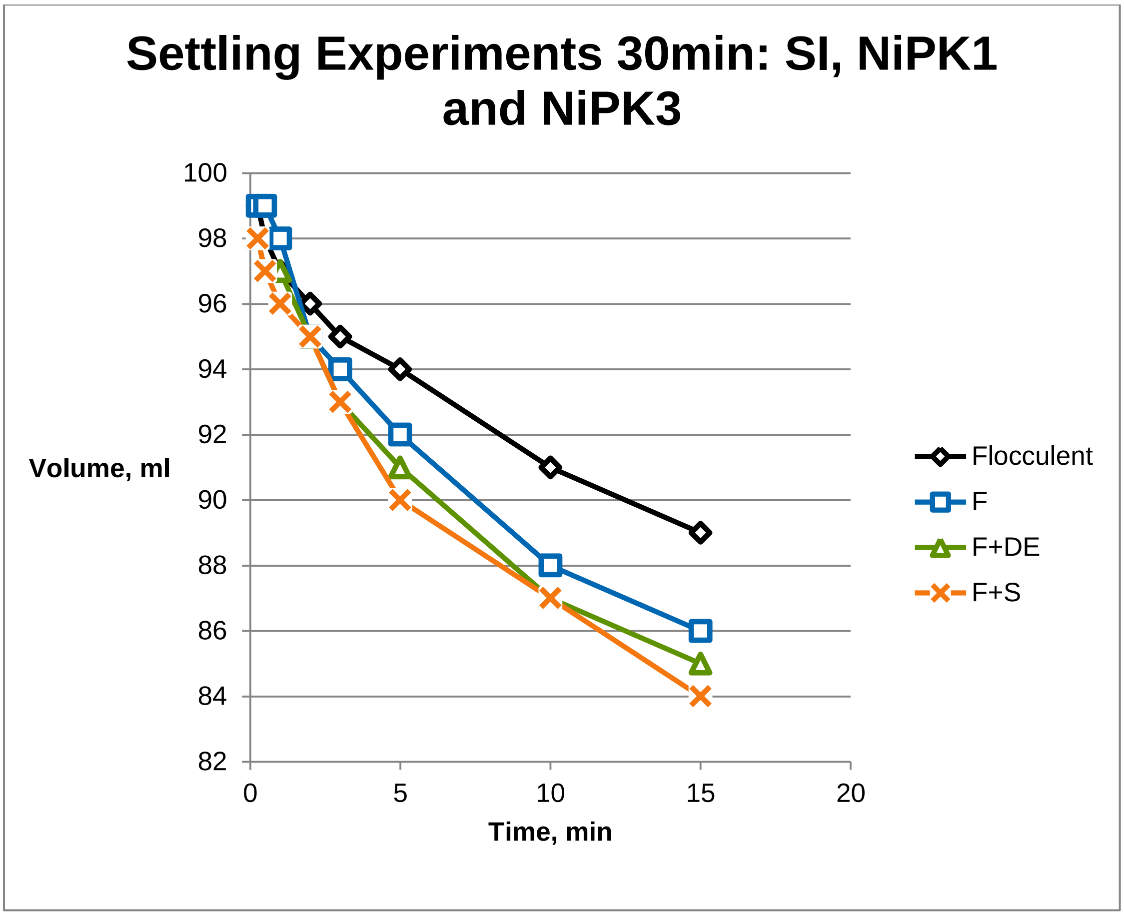


Figure 24. The Settling of SI, NiPK1 and NiPK3 30 min Reaction Time 9.4.2014

Table 20. Concentrations of Cobalt and Nickel after Settling Experiment SI and NiPK1 and NiPK3 30min Reaction Time

	Flocculent	F	F+DE	F+S	Original
Co (mg/l)	0,178	0,138	0,053	0,216	0,246
Ni (mg/l)	12,951	9,616	1,218	18,83	31,119

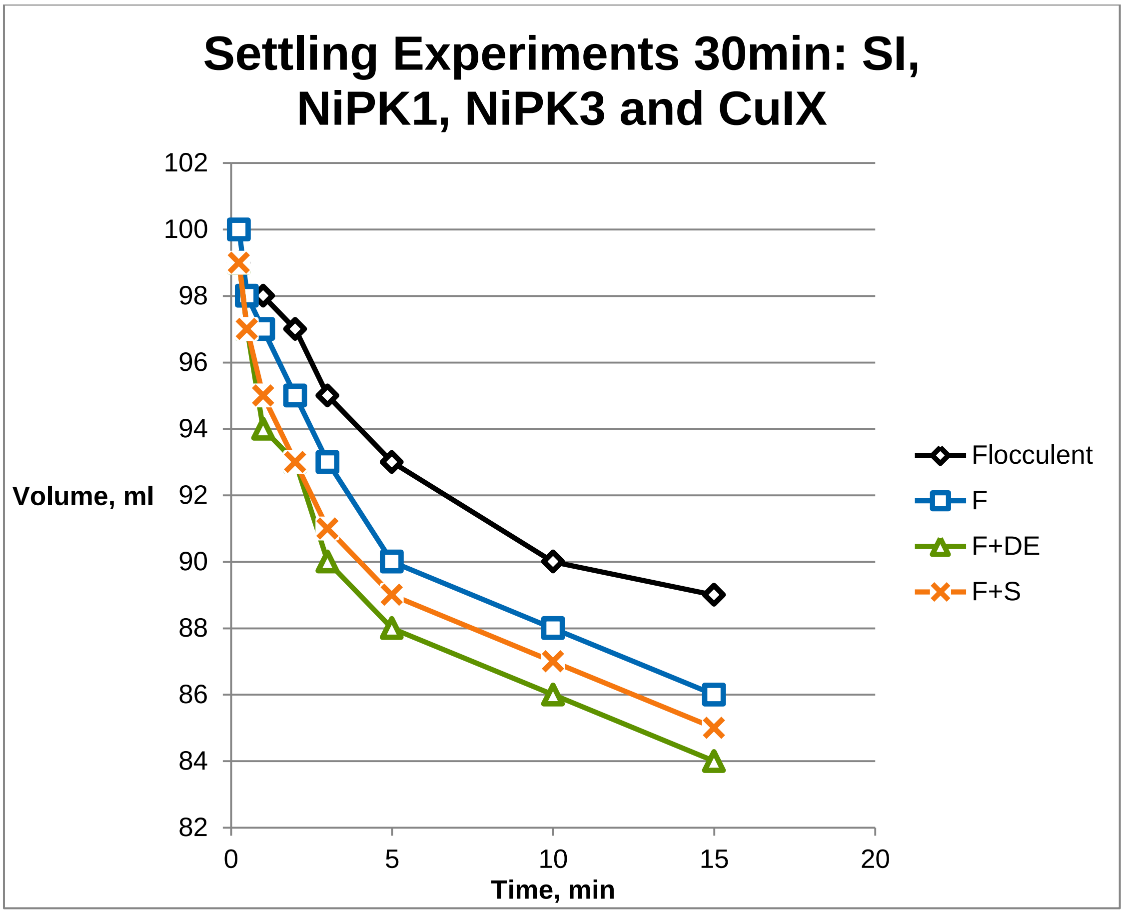


Figure 25. The Settling of SI, NiPK1, NiPK3 and CuIX 30min Reaction Time 10.4.2014

Table 21. Concentrations of Cobalt and Nickel after Settling Experiment SI and NiPK1, NiPK3 and CuIX 30min Reaction Time

	Flocculent	F	F+DE	F+S	Original
Co (mg/l)	0,255	0,361	0,323	0,327	0,467
Ni (mg/l)	10,212	14,886	13,309	14,727	31,659

From the figures can be seen that the 30min reaction time with ferric sulphate and the mixture did not affect to the settling of the samples compared to the settling experiments done before. As can be seen from the figures, the settling was poorest in all the experiments when only the flocculent was used. The presence of diatomite and sand improved the settling compared to the usage of only ferric sulphate. Nickel and cobalt concentrations varied slightly but the best results were gained almost in all the experiments with diatomite. Comparison with the previous results showed that the longer reaction time with ferric sulphate improved the settling and the concentrations of nickel and cobalt were smaller. Extended time made the results also more reliable and logical.

7.3 Silica Sand as a Settling Agent in the Production Scale

Silica sand was supposed to be examined in the production scale for three weeks with different dosages supplied to the precipitation reactor RE 3703. First dosage was calibrated to be 5,1kg/h and this test started on Monday 7.4.2014. The second dosage was 15,3kg/h and this test started on Monday 14.4.2014. The second test was stopped on Wednesday 16.4.2014 because the sand accumulated to the bottom of the third sedimentation reactor RE 3703. The experiment was stopped on Wednesday 16.4.2014 after one and half week of sand feeding. There were no realistic results from the sand feeding in production scale because the sand accumulated to the bottom of the third precipitation reactor and did not enter to the thickener. There might have occurred some settling of cobalt and nickel but they had accumulated to the bottom of the precipitation reactor as well.

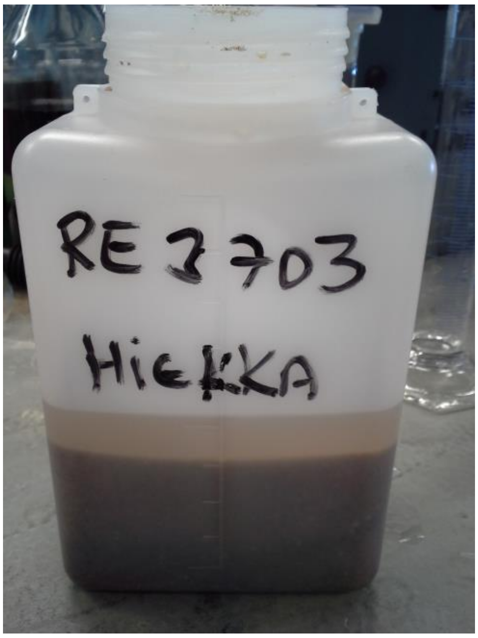


Figure 25. Sand Collected from the Bottom of Precipitation Reactor RE 3703

8 CONCLUSIONS

The purpose of this thesis was to examine the solubilities of cobalt and nickel in carbonate –and hydroxide precipitation, and whether the effectiveness of removing cobalt and nickel from a wastewater could be improved by using alternative settling agents.

The results from the precipitation experiments showed that precipitation started in carbonate precipitation between pH 7 and 8 and in hydroxide precipitation pH 8. The optimal pH was for carbonate precipitation 10 and for hydroxide precipitation it was 11,5. In the hydroxide precipitation both cobalt and nickel dissolved back when the pH was raised above 12,5.

The results from the settling experiments showed that in the first settling experiments the reaction time for the settling agent and the solution was uncertain. The results from the later settling experiments were more logical. Especially in the later settling experiments with a longer reaction time diatomite was clearly the best settling agent. The results with the different dosages of diatomite affected only little to the settling results but the best results were gained with bigger dosages. The examination of diatomite as a settling agent could be continued in the future both in laboratory scale as in production scale. The effectiveness of bentonite as a settling agent was not examined during the preparation of this thesis but results gained elsewhere show that bentonite could improve the settling and thus the examination of bentonite could also be done in Norilsk Nickel Harjavalta Oy.

Part of the experiments was to examine if new fractions (NiPK1, NiPK3 and CuIX) could be steered to the water treatment plant after their carbonate precipitation. The results showed that the difference between standard input water only and standard input waters with NiPK1 and NiPK3 did not alter much. The examination of NiPK1 and NiPK3 joined with standard input waters could be continued in the future. CuIX fraction was not so promising in the results and the idea of joining CuIX to the standard input water could abandon. CuIX fraction portions are occasional and small, about 10m^3 every three weeks.

The experiment in the production scale with silica sand did not work probably because the mass of sand grains was too big and thus the sand accumulated to the bottom of the precipitation reactor.

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APPENDIX 1

RESULTS OF THE PRECIPITATION EXPERIMENTS

Carbonate precipitation 11.3.2014

Experiment	**pH**	**Na_2CO_3 (196g/l) addition (ml)**	**Co (mg/l)**	**Ni (mg/l)**
A1.1	7	0,2	1024,2	1731,9
A1.2	8	16,1	126,24	159,16
A1.3	8,5	3,5	16,63	22,25
A1.4	8,75	1,5	13,17	17,97
A1.5	9	1,5	4,35	5,49
A1.6	9,25	2,4	2,50	2,91
A1.7	9,5	3,5	1,51	1,52
A1.8	9,75	5,7	1,25	1,19
A1.9	10	14,0	0,99	0,80

Hydroxide precipitation 12.3.2014

Experiment	**pH**	**NaOH (330g/l) addition (ml)**	**Co (mg/l)**	**Ni (mg/l)**
A2.1	7	0,1	998,5	925,2
A2.2	8	66,4	252,7	119,4
A2.3	9	18	4,02	0,96
A2.4	9,5	1,5	0,99	0,28
A2.5	9,75	1,2	0,44	0,15
A2.6	10	1	0,17	0,15
A2.7	10,25	1,5	0,073	0,063
A2.8	10,5	1,4	0,050	0,064
A2.9	10,75	1,7	0,20	2,98
A2.10	11	2,8	0,026	0,053
A2.11	11,5	9,0	0,021	0,019
A2.12	12	12,6	0,035	0,018
A2.13	12,5	17,8	0,049	0,028
A2.14	13	34	0,78	1,61

Carbonate –and hydroxide precipitation 14.3.2014

Experiment	**pH**	**Na_2CO_3 (196g/l) addition (ml)**	**Co (mg/l)**	**Ni (mg/l)**
A3.1	7	0,2	981,7	902,9
A3.2	8	26	151,7	169,7
A3.3	9	7,8	10,98	13,63
A3.4	9,5	7,6	4,84	4,60
A3.5	9,75	10	1,96	0,44
A3.6	10	30	2,64	0,46
		NaOH (360g/l) addition (ml)		
A3.7	10,25	2,4	0,38	0,33
A3.8	10,5	2,7	0,25	0,18
A3.9	10,75	1,0	0,10	0,081
A3.10	11	0,6	0,034	0,032
A3.11	11,25	0,5	0,025	0,016
A3.12	11,5	0,7	0,033	0,119
A3.13	12	2,1	0,031	0,018
A3.14	12,5	13	0,039	0,009
A3.15	13	32	0,13	0,008

RESULTS FROM THE SETTLING EXPERIMENTS NIPK1, NIPK3 AND CUIX

Settling experiments: CuIX 17.3.2014

Original Co/Ni concentration CuIX Co:53,19mg/l and Ni: 0,36mg/l					
Experiment	Settling agent	Dosage	Co (mg/l)	Ni (mg/l)	Observations
B1.1	F	50l/h	0,53	1,66	Flocks are formed, really slow settling, solution turbid
B1.2	S1	10kg/h	0,48	1,36	Small flocks, quite clear solution, slow settling
B1.3	S2	25kg/h		2,39	Did not settle properly
B1.4	DE1	10kg/h	2,08	0,048	Clear, flocks did not settle properly, small flocks
B1.5	DE2	25kg/h	1,82	0,045	Quite large flocks, more turbid than diatomite 10kg/h, did not settle properly

Settling experiments: NiPK3 20.3.2014

Original Co/Ni concentration NiPK3 Co: 25,12mg/l and Ni: 0,32mg/l					
Experiment	Settling agent	Dosage	Co (mg/l)	Ni (mg/l)	Observations
B2.1	F	50l/h	0,13	0,040	Settled slowly, quite turbid
B2.2	S1	10kg/h	1,54	4,85	Quite clear, flocks settled slowly
B2.3	S2	25kg/h	0,20	0,26	Quite clear, flocks are fluffy
B2.4	DE1	10kg/h	0,28	0,63	Quite clear, flocks were formed but the smallest flocks did not settle well
B.5	DE2	25kg/h	0,28	0,54	Quite clear, flocks settled first well but some of them did not settle

Settling experiments: NiPK1 24.3.2014

Original Co/Ni concentration NiPK1 Co: 29,96mg/l and Ni: 0,51mg/l					
Experiment	Settling agent	Dosage	Co (mg/l)	Ni (mg/l)	Observations
B3.1	F	50l/h		0,064	Sample is turbid, flocks are formed well, settling slowly
B3.2	S1	10kg/h	0,60	0,0039	Almost completely clear, flocks really small
B3.3	S2	25kg/h	0,76	0,0042	Quite clear, flocks quite small and fluffy
B3.4	DE1	10kg/h	1,35	0,54	Sample quite clear, small flocks
B3.5	DE2	25kg/h			Sample quite clear, small flocks

APPENDIX 3

RESULTS FROM THE SETTLING EXPERIMENTS SI, NIPK1, NIPK3 AND CUIX

Settling experiments: Standard Input waters 27.3.2014

Original Co/Ni concentration Co: 5,69mg/l and Ni: 6,17mg/l						
Experiment	Settling agent	Dosage	Co (mg/l)	Ni (mg/l)	Sediment bed (ml)	Observations
C1.1	F	50kg/h	0,18	0,65	10	Sample was turbid, big flocks, small flocks settled slowly
C1.2	DE1	5kg/h	0,65	0,74	2	Quite turbid, but clearer than ferric sulphate, flocks settle slowly
C1.3	DE2	15kg/h	0,57	0,66	1	Quite turbid, flocks are formed well
C1.4	DE3	25kg/h	0,29	0,30	2	Quite turbid, flocks are formed well
C1.5	S1	5kg/h	0,85	1,02	1	Turbid, flocks are formed well
C1.6	S2	15kg/h	1,06	1,29	1	Turbid, flocks are formed well, fluffy flocks did not settle
C1.7	S3	25kg/h	1,14	1,41	2	Sample more turbid than sand 15kg/h, fluffy flocks did not settle

Settling experiments: SI and NIPK1 2.4.2014

Original Co/Ni concentration Co: 0,45mg/l and Ni: 10,94mg/l						
Experi-ment	Settling agent	Dosage	Co (mg/l)	Ni (mg/l)	Sediment bed (ml)	Observations
C2.1	F	50l/h	0,17	0,92	9	Sample turbid, large flocks settled well, small settle slowly
C2.2	DE1	5kg/h	0,15	1,38	5	Sample was first turbid, large flocks settled well, small and fluffy didn't
C2.3	DE2	15kg/h	0,15	1,40	4	Quite turbid, large flocks settled well, small didn't
C2.4	DE3	25kg/h	0,14	1,53	4	Quite turbid, large flocks settled well, small didn't
C2.5	S1	5kg/h	0,14	1,52	5	First turbid, flocks were formed well, fluffy flocks didn't settle
C2.6	S2	15kg/h	0,15	1,63	5	First turbid, flocks were formed well, fluffy flocks didn't settle
C2.7	S3	25kg/h	0,17	1,8	5	Turbid, flocks formed well but fluffy flocks didn't settle

Settling experiments: SI and NiPK3 31.3.2014

Original Co/Ni concentration Co: 3,09mg/l and Ni: 9,27mg/l						
Experi-ment	Settling agent	Dosage	Co (mg/l)	Ni (mg/l)	Sediment bed (ml)	Observations
C3.1	Ferric sulphate	50l/h	0,18	0,422	7	Quite turbid, flocks were formed well
C3.2	Diatomite	5kg/h	0,36	5,29	2	First turbid, large flocks settled well, but fluffy flocks didn't, in the end clear
C3.3	Diatomite	15kg/h	0,27	3,79	2	Quite turbid, large flocks settled, fluffy flocks didn't
C3.4	Diatomite	25kg/h	0,27	4,11	3	Quite turbid first, large flocks were formed
C3.5	Silica sand	5kg/h	0,44	8,48	3	Quite clear, didn't settle well, flocks were small and fluffy
C3.6	Silica sand	15kg/h	0,57	10,46	4	First flocks were large, and settled well. quite clear, fluffy flocks didn't settle
C3.7	Silica sand	25kg/h	0,52	10,34	4	First turbid and large flocks, in the end clear

Settling experiments: SI, NiPK1 and NiPK3 3.4.2014

Original Co/Ni concentration Co: 1,70mg/l and Ni: 9,84mg/l						
Experiment	Settling agent	Dosage	Co (mg/l)	Ni (mg/l)	Sediment bed (ml)	Observations
C4.1	F	50l/h	0,32	4,63	8	Sample turbid, large flocks were formed, Settled slowly
C4.2	DE1	5kg/h	0,25	4,80	5	First turbid, large flocks, fluffy flocks didn’t settle
C4.3	DE2	15kg/h	0,23	4,40	6	First large flocks and turbid, fluffy flocks didn’t settle
C4.4	DE3	25kg/h	0,26	5,43	5	Large flocks settled well, fluffy flocks didn’t
C4.5	S1	5kg/h	0,37	9,16	6	Large flocks were formed and settled well, fluffy flocks didn’t
C4.6	S2	15kg/h	0,35	7,91	5	Large flocks settled, fluffy flocks didn’t
C4.7	S3	25kg/h	0,30	6,85	6	Large flocks settled, fluffy flocks didn’t

Settling experiments: SI, NiPK1, NiPK3 and CuIX 4.4.2014

Original Co/Ni concentration Co: 0,564 and Ni: 10, 57mg/l						
Experiment	Settling agent	Dosage	Co (mg/l)	Ni (mg/l)	Sediment bed (ml)	Observations
C5.1	F	50l/h	0,36	5,82	9	Turbid, flocks were formed but settled weakly
C5.2	DE1	5kg/h	0,23	4,44	8	First turbid and large flocks, fluffy flocks didn’t settle
C5.3	DE2	15kg/h	0,25	5,41	6	First turbid, large flocks, didn’t settle well
C5.4	DE3	25kg/h	0,22	4,58	5	First large flocks, turbid, settled weakly
C5.5	S1	5kg/h	0,26	5,83	5	First turbid, large flocks are formed and settle well, fluffy flocks left and didn’t settle
C5.6	S2	15kg/h	0,29	6,49	7	Turbid, fluffy flocks didn’t settle
C5.7	S3	25kg/h	0,31	7,49	7	Turbid, fluffy flocks didn’t settle

RESULTS FROM THE SETTLING EXPERIMENTS SI, NIPK1, NIPK3 AND CUIX 30MIN REACTION TIME WITH FERRIC SULPHATE

Settling experiments: Standard Input waters 30min reaction time 8.4.2014

	Original Co/Ni concentration Co: 0,62mg/l and Ni: 85,20mg/l					
Experi-ment	**Settling agent**	**Dosage**	**Co (mg/l)**	**Ni (mg/l)**	**Sediment bed (ml)**	**Observations**
D1.1	Flocculent	1,5g/m³	0,20	8,77	3	Flocks are formed, larger settle, quite turbid, fluffy flocks didn't settle
D1.2	F	50ml/h	0,18	13,92	8	Large flocks were formed, fluffy flocks didn't settle, quite turbid
D1.3	F+DE	50l/h + 15kg/h	0,17	13,61	6	Turbid, large flocks, small flocks didn't settle
D1.4	F+S	50l/h + 15kg/h	0,20	19,90	7	Large flocks, fluffy flocks didn't settle

Settling experiments: SI and NiPK1 30min reaction time 16.4.2014

	Original Co/Ni concentration Co: 0,55mg/l and Ni: 32,11mg/l					
Experi-ment	**Settling agents**	**Dosage**	**Co (mg/l)**	**Ni (mg/l)**	**Sediment bed (ml)**	**Observations**
D2.1	Flocculent	1,5g/m³	0,19	8,60	4	Large flocks were formed, Quite turbid, small flocks didn't settle
D2.2	F	50l/h	0,11	10,11	6	Turbid, settled slowly, flocks were large
D2.3	F+DE	50l/h + 15kg/h	0,082	6,51	10	Turbid, large flocks, settled slowly
D2.4	F+S	50l/h + 15kg/h	0,12	12,26	8	Turbid, large flocks, fluffy flocks didn't settle, sediment bed was high first

Settling Experiments: SI and NiPK3 30min reaction time 15.4.2014

	Original Co/Ni concentration Co: 0,41mg/l and Ni: 31,21mg/l					
Experiment	**Settling agent**	**Dosage**	**Co (mg/l)**	**Ni (mg/l)**	**Sediment bed (ml)**	**Observations**
D3.1	Flocculent	1,5g/m^3	0,20	13,79	3	Quite clear, fluffy flocks didn't settle
D3.2	F	50ml/h	0,23	24,74	2	Quite turbid, large flocks, didn't settle well
D3.3	F+DE	50l/h + 15kg/h	0,16	12,41	7	Quite turbid, settled slowly
D3.4	F+S	50l/h + 15kg/h	0,18	14,58	9	Turbid, Fluffy flocks didn't settle well

Settling experiments: SI, NiPK1 and NiPK3 30min reaction time 9.4.2014

	Original Co/Ni concentration Co: 0,25mg/l and Ni: 31,12mg/l					
Experiment	**Settling agent**	**Dosage**	**Co (mg/l)**	**Ni (mg/l)**	**Sediment bed (ml)**	**Observations**
D4.1	Flocculent	1,5g/m^3	0,18	12,95	5	Large flocks were formed, small flocks didn't settle, quite turbid
D4.2	F	50l/h	0,14	9,61	9	Large flocks, didn't settle well, turbid
D4.3	F+DE	50l/h + 15kg/h	0,053	1,22	10	First sediment bed high (15ml), fluffy flocks didn't settle
D4.4	F+S	50l/h + 15kg/h	0,22	18,83	9	Large flocks, turbid

Settling experiments: SI, NiPK1, NiPK3 and CuIX 30min reaction time 10.4.2014

	Original Co/Ni concentration Co: 0,47mg/l and Ni: 31,66mg/l					
Experi-ment	**Settling agent**	**Dosage**	**Co (mg/l)**	**Ni (mg/l)**	**Sediment bed (ml)**	**Observations**
D5.1	Flocculent	1,5g/m³	0,26	10,21	5	Quite clear, large fluffy flocks, didn't settle well
D5.2	F	50l/h	0,36	14,89	8	Large flocks, fluffy small flocks didn't settle
D5.3	F+DE	50l/h + 15kg/h	0,32	13,31	9	Large flocks, fluffy small flocks didn't settle
D5.4	F+	50l/h + 15kg/h	0,33	14,73	9	Turbid, large flocks, fluffy flocks didn't settle